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NAME OF SUPERVISOR/NOM DU DIRECTEUR DE THÈSE D.L. Flock

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THE USE OF SODIUM HYDROXIDE SLUGS TO
IMPROVE THE WATER FLOOD RECOVERY
OF VISCOUS CRUDE OILS

by



HARVEY D. GARDINER

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
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THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "The USE OF SODIUM HYDROXIDE SLUGS TO IMPROVE THE WATER FLOOD RECOVERY OF VISCOUS CRUDE OILS", submitted by Harvey D. Gardiner, in partial fulfilment of the requirements for the degree of Master of Science in Petroleum Engineering.

Supervisor

h. P. Lewis

External Examiner

Date April 22, 1977

ABSTRACT

An experimental study was conducted to investigate the effects on water flood recovery caused by adding sodium hydroxide to a portion of the injected fluids. The investigation was conducted using actual reservoir fluids from the Lloydminster area in an unconsolidated porous medium.

Measurement of the sand and fluid properties indicated that sodium hydroxide caused a reduction of the oil-water interfacial tension and a shift in the system wettability from oil wet to neutral or water wet.

The addition of sodium hydroxide in concentrations greater than 0.1 percent by weight to all of the injected fluid (brine) resulted in recoveries of approximately 45 percent of the initial oil-in-place at a water-oil ratio of 10. Flooding with pure water resulted in recoveries of approximately 22.5 percent.

Results of the displacement tests using various size slugs of 0.1 percent sodium hydroxide indicated that slugs of approximately 0.4 pore volumes were required to obtain recoveries equivalent to adding sodium hydroxide to all of the injected fluid.

Monitoring of the pH of the effluent from the sand packs indicated that the sodium hydroxide slugs

were diluted by fingering of the untreated brine at the trailing edge. Higher concentrations of sodium hydroxide compensated for the dilution and fingering, increasing the recoveries for smaller slug sizes.

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INTRODUCTION

Significant reserves of heavy crude oils are located in Western Canada. Using conventional methods of recovery, these reserves can only be partially recovered. Westfall⁴⁹ states that approximately 5 to 6 percent of the oil is recoverable by primary methods and 10 to 12 percent is recoverable by water flood. With the increasing world demand for oil an efficient economical method is required for the recovery of heavy crude oils.

Several previous studies have been conducted at the University of Alberta on methods of improving recoveries from viscous crude systems. Collins⁹ investigated the influence of viscosity ratio on the recovery efficiency of viscous crude oil in long unconsolidated sand packs using a native brine.

Scott⁴⁰ studied the suitability of adding different acids and bases to the water when flooding crude oil reservoirs. He found that a low concentration of sodium hydroxide would reduce water-oil interfacial tension, cause an oil-wet sand to become more water-wet and significantly increase oil recovery.

Fazil²⁰ investigated the effect of carbonated brine on the recovery of viscous crude oil. He obtained significant increases in recovery, which he attributed

to the reduction of crude oil viscosity and oil-water interfacial tension.

Scott⁴¹ studied the effects of different chemicals on water flood recovery of viscous crude oil. He found that recovery could be significantly increased by the injection of a 0.1 percent by weight or greater concentration of sodium hydroxide in brine. He indicated that the sodium hydroxide requirements are greatly reduced if sodium chloride was added to the injection fluid.

The addition of chemicals to only a portion of the injected fluid has been investigated by several authors^{30,37,43}. They found that a small slug of a chemical solution, if properly designed, can achieve similar recoveries to water floods which have the chemical added to the entire injected fluid.

The purpose of this study was to investigate the effect on viscous crude oil recovery of adding sodium hydroxide to only a portion of the displacing water. Reservoir conditions typical of the Lloydminster Sparky heavy crude oil reservoirs were duplicated where possible.

LITERATURE REVIEW

Chemical Water Flooding

Early investigations of the use of chemical additives to improve water flood recovery were done by Nutting³⁶ in 1923, Uren and Fahmy⁴⁶ in 1927 and Beckstrom and Van Tuyl⁴ in 1927.

Nutting suggested that there was an attraction between the silica particles (SiO_2) and the hydrogen ions in the water which would lead to the formation of a layer of siloxyl radicals (SiOOH) on the rock surface. The acidic siloxyl was thought to react with the basic constituents of the oil to form a stable oil layer on the rock surface. He theorized that if a strong base was added to the displacing water it would replace the weaker base (oil) siloxyl radical on the rock's surface and improve the recovery.

Beckstrom and Van Tuyl⁴ performed displacement tests on sand cores and concluded that only strong bases and weak acids were effective as water flooding additives. Uren and Fahmy⁴⁶ confirmed this conclusion and attributed the increase in recovery to a reduction in interfacial tension between the oil and water. They suggested that there was also a reduction in interfacial tension between the water and rock due to a reaction

at the rock surface.

Bartell and Miller³ found that the addition of inorganic chemical additives produced equivalent recoveries in a water-oil system and a water-benzene system although the interfacial tensions of the two systems were quite different. They concluded that recoveries were increased by altering the rock-water interface and that the altering of the oil-water interface did not have a significant effect.

Terwilliger and Yuster⁴⁵ were the first to differentiate between surface active and surface inactive agents. Surface active agents or surfactants are usually polar-nonpolar molecules which concentrate at interfaces and lower the interfacial tension. Surface inactive additives such as sodium hydroxide, sodium carbonate, and sodium sulfite do not lower the interfacial tension as much as surface active additives. The surface inactive additives advantage is that they are not adsorbed to the same extent as surface active compounds since they do not concentrate at the interfaces. Terwilliger and Yuster⁴⁵ found that a 0.1 percent by weight sodium hydroxide solution could reduce residual oil saturation in cores that were previously water flooded from 52 percent to 35 percent.

Calhoun et al.⁷ conducted a series of tests on

Bradford sand cores using sodium hydroxide as an additive in the displacing water. In all cases, the residual oil saturations after flooding with water containing sodium hydroxide (0.5 percent by weight) were lower than those obtained for equivalent floods using water. The increase in recovery was attributed to a decrease of interfacial tensions and a change in wettability. The decrease of interfacial tensions was said to be caused by the formation of surface active groups as a result of the reaction of sodium hydroxide with the polar compounds in the crude oil. It was noted that the use of chemicals such as sodium hydroxide which are not surface active additives, can lower interfacial tensions without great losses due to adsorption observed when using surface active agents.

Reisberg and Doscher³⁹ conducted tests on Ventura crude oil, to find the effect of pH on the oil water interface. They found that weak sodium hydroxide solutions would displace the oil from the surface of a glass slide, whereas a weak solution of hydrochloric acid, having the same interfacial tension to oil, would displace little of the oil. This was attributed to the presence of rigid films at the oil-water interface which are stable in the presence of an acidic aqueous phase, but broke down in the presence of an alkaline aqueous phase.

The rigid film was isolated and found to be a highly oxygenated, low molecular weight constituent of the resins and asphaltenes. This was in agreement with earlier investigations^{15,17,18} which suggested that porphyrins with heavy metal molecules attached were the main cause of the rigid films in asphaltic crude oils. Reisberg and Doscher³⁹ concluded that the reduction of interfacial tension and changes in wettability were due to a component of the oil which was initially positively adsorbed at the oil-water-solid interface. The component, when dissolved in the aqueous phase by interaction with the basic sodium hydroxide, changes the surface forces of the aqueous phase.

The increase in recovery due to the alkaline solution occurred after the breakthrough of the front. This was attributed to adsorption and reaction at the sand surface reducing the concentration of the sodium hydroxide at the flood front as it moved through the reservoir. They suggested that the increase in recovery was not due just to the reduction of the oil-water interfacial tension but also to a change in the oil-solid and water-solid interfacial tension.

Dunning and Johanson¹⁸ found that the displacement efficiency of inorganic solutions such as those containing sodium hydroxide (builders) are dependent

upon the pH of the solutions. They attributed the reduction in interfacial tension to a chemical reaction on the sand surface that caused an irreversible adsorption of the sodium hydroxide. Dunning and Johanson¹⁸ compared displacement efficiencies of inorganic additives with other additives and found them surpassed only by expensive nonionic surfactants.

Scott⁴⁰ conducted displacement tests using dilute sodium hydroxide solutions to displace viscous crude (Lloydminster) in unconsolidated packs of Sparky sand. Flooding with sodium hydroxide changed the sand from a neutral or partially oil-wet state to a water-wet state and drastically lowered the interfacial tensions. Sodium hydroxide concentrations of 0.005 percent and 0.001 percent by weight produced recoveries of 50.8 and 56.2 percent of the initial oil in place respectively, compared to 39.9 percent recovered by injecting brine. Scott⁴⁰ noted that there was a delay between the time the front passes through the reservoir and the increase in recovery. He suggested that this was due to dilution and fingering preventing the sodium hydroxide from fully contacting the rock surfaces.

Scott⁴¹ investigated the use of chemical additives to improve the water flood recovery of viscous crudes. He ran tests on Lloydminster crude in

short core packs of unconsolidated Sparky sand. Sodium hydroxide in brine solution of 0.1 percent by weight was found to result in the most efficient recoveries. A larger concentration did little to increase recovery whereas a lower concentration resulted in a decreased recovery. The presence of sodium chloride helped reduce the amount of sodium hydroxide required.

Scott⁴¹ suggests that the displacement took place by an emulsion slug mechanism. Dilution and reaction at the leading edge of the injected chemical front lead to the formation of an emulsion which would reduce the conductivity of the flow path. The reduced conductivity in the flow path would force the water to flow through the next path of least resistance. The emulsified water would flow only when all the paths of least resistance were blocked. The emulsion would move as a front and because of its low mobility (and thus a more favorable mobility ratio) would more efficiently displace the oil.

Cooper¹¹ ran sodium hydroxide displacement tests on Lloydminster crude oil in Berea sandstone cores. He found that the recovery using a 0.2 percent by weight sodium hydroxide solution increased with temperature to a much greater degree than equivalent floods using distilled water. This was attributed to

the interfacial tension reduction caused by the sodium hydroxide being sensitive to temperature. Cooper correlated interfacial tension with sodium hydroxide concentration and found that it reached a minimum between 0.1 and 0.3 percent sodium hydroxide by weight. Monitoring of the effluent pH indicated that 0.1 pore volume of water was produced before the pH increased to that of the injected water. This delayed increase in pH suggests that sodium hydroxide was adsorbed in the system.

Ehrlich et al.¹⁹ investigated the use of sodium hydroxide in light oil reservoirs to change both wettability and interfacial tension in order to increase oil recovery. They concluded that increased recovery was due to a wettability alteration. Also, they concluded that if the interfacial tension was lowered enough it would also increase recovery. They found that in a wettability alteration water flood recovery was not rate dependent but was significantly affected by how early in the water flood sodium hydroxide was injected. Initiating sodium hydroxide injection early in the life of the water flood greatly increased recoveries. When interfacial tension alteration was the primary mechanism, recovery was highly rate dependent but did not depend on the state of depletion of the reservoir when the sodium hydroxide was injected. They stated that to predict the effect of sodium hydroxide

on water flood recovery, the interfacial tension and compatability of the sodium hydroxide to the formation should be tested. Laboratory water floods of reservoir cores were also recommended.

Jennings et al.²⁷ conducted an investigation of the use of sodium hydroxide to improve water flood recovery of viscous crudes in water-wet porous media. They stated that the addition of sodium hydroxide to the flood water reduced the interfacial tension between the oil and water (sodium hydroxide reacted with the carboxylic acid in the oil to reduce interfacial tension). If the tension was lowered below 0.1 dyne/cm increased recoveries were obtained. Jennings et al.²⁷ also stated that the addition of sodium hydroxide to the water flood reduced the quantity of sodium hydroxide required but due to the larger amounts of sodium chloride required it was concluded to be uneconomical.

Jennings et al.²⁷ suggested that lowering the interfacial tension resulted in the formation of an emulsion that due to its lowered mobility could sweep the reservoir more efficiently than a conventional water flood. They based this theory on the fact that when oil-in-water emulsions induced by sodium hydroxide were injected into the reservoir recovery was increased significantly.

Jennings et al.²⁷ found that a 15 percent pore volume slug of 0.5 percent by weight sodium hydroxide obtained similar recoveries to the continuous injection of 0.5 percent by weight sodium hydroxide.

A field test²⁶ using sodium hydroxide in a watered out portion of the Muddy J sand of the West Harrisburg Nebraska field produced a significant amount of oil. The reservoir was oil-wet prior to the test and was changed to preferentially water-wet by the sodium hydroxide.

A field trial of the caustic flooding process was conducted on the viscous crude Whittier Field in Whittier, California. More oil was produced than would have been produced from a continuous water flood. Caustic also appeared to improve the injectivity of the injection wells.

Slug Flooding

Early investigators of chemical water flooding assumed that it was necessary to add the chemical additive to all of the water injected. In 1952 Preston and Calhoun³⁷ suggested that only a part of the injected water be treated. It was suggested that an injected slug of surfactant solution would form a narrow band

which could be pushed through the reservoir by untreated water. As the band of surfactant or chemically treated water passed through the reservoir it would release the oil from the rock and drive the oil ahead of it. They stated that movement of the surfactant slug through the reservoir could be described by the application of the theory of chromatography, although they presented no experimental evidence to support this mechanism.

Chromatography is a technique used to separate components in a mixture by utilizing the selective adsorption phenomenon of a porous medium. When a solution of concentration C_0 flows through a porous medium, the solute is adsorbed and the solvent moves ahead at a higher velocity. The solute remains in the solution only where porous surfaces are saturated with solute. This causes an adsorption zone which progresses through the porous medium at a slower velocity than the solvent. When pure solvent is injected behind the slug a trailing mixing zone develops, separating the pure solvent from the slug.

The shape of the advancing concentration profile is determined by the kinetics of adsorption. If the adsorption equilibrium occurs at a finite rate, both leading and trailing edges are diffuse. The size of the slug zone increases and the concentration

decreases as it progresses through the reservoir (see Figure 1-1).

If the adsorption equilibrium is instantaneous, the concentration profile depends upon the shape of the adsorption isotherm as illustrated in Figure 1-2. The adsorption isotherm is the equilibrium relationship between the amount of solute adsorbed and the amount in the solution. One procedure to obtain the adsorption isotherm, described by Preston and Calhoun³⁷, is to establish a known concentration in a solution and the difference in concentration of the solute before and after it contacted the porous media would be the amount adsorbed by the porous media. If this procedure is followed several times with different concentrations of solute an adsorption curve can be constructed.

Preston and Calhoun³⁷ rearranged DeVault's¹⁴ basic equations of chromatography to obtain equations 1-1, 1-2 and 1-3, which describe the position of the leading edge of the slug, position of the trailing edge of the slug and the minimum effective slug size.

$$x_d = \frac{v_t}{A\phi} \left[\frac{1}{1 + \left(\frac{1-\phi}{\phi} \right) \rho \left(\frac{f(C_0)}{C_0} \right)} \right] \quad 1-1$$

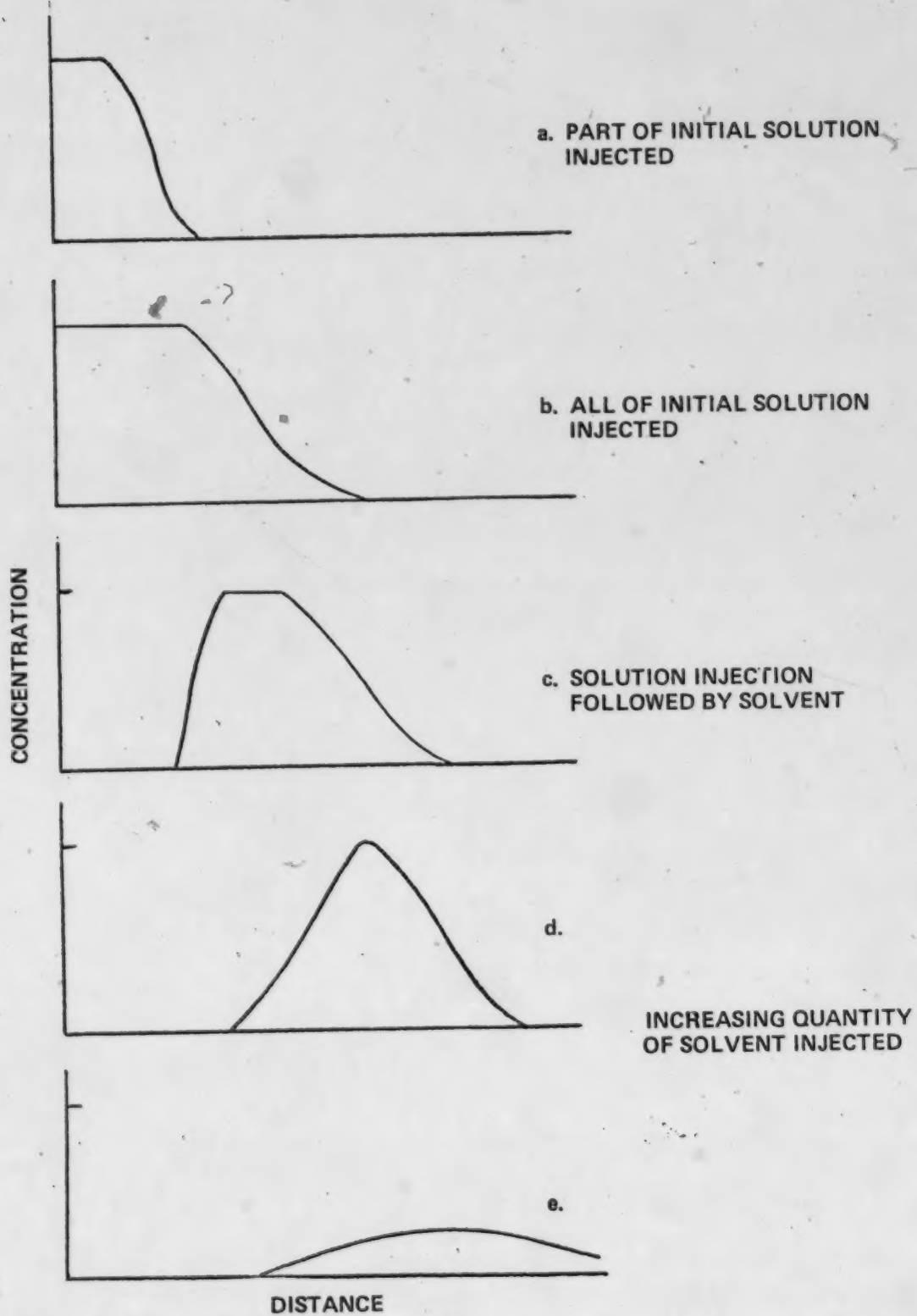
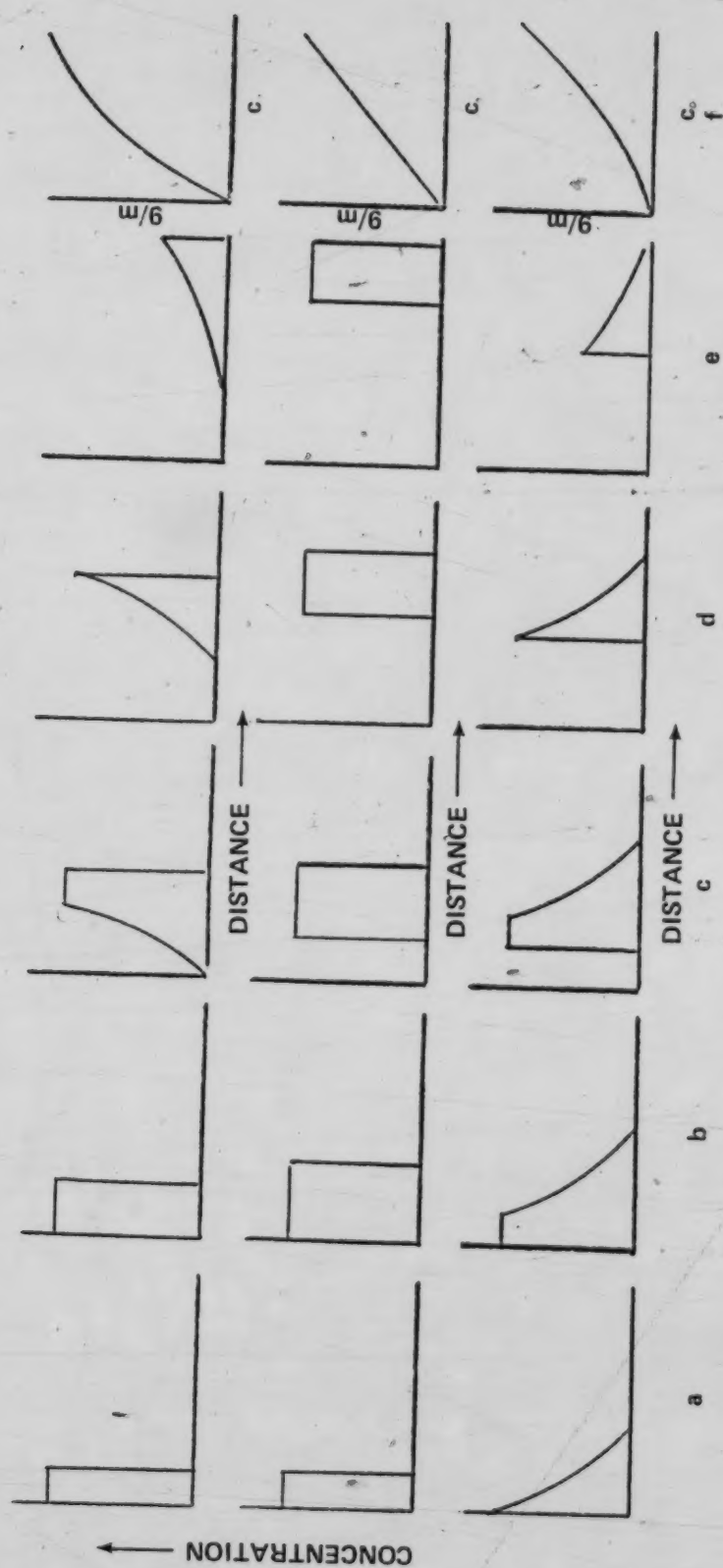


FIGURE 1-1 SCHEMATIC REPRESENTATION OF THE MOVEMENT OF AN NON-INSTANTANEOUS EQUILIBRIUM ADSORPTION ZONE



- a. PART OF INITIAL SLUG INJECTED
- b. ALL OF INITIAL SLUG INJECTED
- c, d, e. INCREASING VOLUME OF SOLVENT INJECTED
- f. ADSORPTION ISOTHERM

FIGURE 1-2 SCHEMATIC REPRESENTATION OF THE MOVEMENT OF AN INSTANTANEOUS EQUILIBRIUM ADSORPTION ZONE

$$X = \frac{V_s}{A\phi} \left[\frac{1}{1 + \left(\frac{1-\phi}{\phi} \right) \rho f'(C)} \right] \quad 1-2$$

$$V_m = X_{dt} A \phi P \left[\frac{f(C_o)}{C_o} - f'(C_o) \right] \quad 1-3$$

Where:

- X_d = distance from injection source to the leading edge of the solution zone, cm,
- X = distance to trailing edge of slug from injection source, cm,
- X_{dt} = total length of adsorbant column, cm,
- V_t = volume of fluids injected ($V_t = V_s +$ volume of displacing fluid), cc,
- V_s = volume of solvent injected, cc,
- V_m = minimum effective slug size, cc,
- A = cross sectional area, cm^2 ,
- ϕ = porosity, fraction,
- ρ = density of adsorbant, gm/cc,
- $f(C_o)$ = function notation for general adsorption isotherm,
- $f'(C_o)$ = first derivative of the general adsorption isotherm,
- P = $\rho (1-\phi)/\phi$.

Johnson³⁰ stated that two assumptions were implicit in the suggestion that a slug could perform as well as continuous injection. First, the time required for the surface active agent to release the oil from any point in the reservoir was less than the time it took for the surfactant bank to pass that point. Second, the released oil must travel faster than the surfactant bank. Johnson³⁰ stated that the second assumption is probably valid. Partially adsorbed surfactant moves much slower than the water eluting it. Thus, the oil would be banked ahead of the water with the solute removed, which in turn moves ahead of the surfactant slug.

Johnson³⁰ extended DeVault's¹⁴ basic equation to obtain an equation for minimum effective slug size

$$V_{\min} = f(C_o)/C_o - f(C_o) \quad 1-4$$

He evaluated the adsorption isotherm by the expression

$$f(C_o) = (N-1)C_o \quad 1-5$$

Where: N = number of pore volumes injected until the surfactant breaks through.

Johnson³⁰ concluded that the best results were

obtained when the surfactant was injected early in the life of the reservoir.

Taber^{43,44} pointed out that the chromatographic theory used by Preston and Calhoun³⁷ assumed that a portion of the slug was full strength until breakthrough. This requires the injection of large quantities of surfactant to account for adsorption and dilution losses.

Taber^{43,44} ran displacement tests at various concentrations which seemed to confirm his theory. He also found that adsorption losses increased with concentrations less than 1000 ppm when using Triton X-100 on Berea sandstone. At concentrations of Triton X-100 greater than 1000 ppm adsorption was insensitive to concentration.

Since slug concentration is directly proportional to the rate of movement of the slug through the reservoir, Taber postulated that a small, high concentration slug would achieve the same results as a large, low concentration slug. This would lead to a rapidly moving slug near the injection well that would move more slowly as its concentration decreased. The rapid movement of the slug through the reservoir results in less dispersion, reducing the amount of water required to push the slug through the reservoir. Moore and Blum³⁴ stated that a high concentration slug is more effective because it

causes a sharp reduction of interfacial tension which is more effective in displacing the oil than a gradual reduction of the interfacial tension typical of dilute solutions.

THEORY

Interfacial Tension, Adhesion, Wettability, and Adsorption

Surface activity in a reservoir is dependent upon the interfacial tension between fluids, and adhesion between the rock and the fluids. Interfacial tension and adhesion are force summations of the interaction of the molecules of two different materials across their interface.

The universal attraction between all molecules is fundamental to all aspects of surface activity. Garrett²² states that all forces between molecules are electrostatic consisting of van der Waal's force of attraction and the Coulombic energy of attraction between ions. An interface is formed between the water and oil because the force of attraction between the water molecules is stronger than the oil-water molecular attraction. This is due to the water molecules being polar and similar in size, whereas the oil molecules vary in size and are generally non-polar. Thus, if an oil molecule becomes immersed among water molecules, it will be expelled since it blocks the attraction between the water molecules.

Miscibility of some hydrocarbon compounds in water is caused by their structural polarity. Some hydrocarbon compounds have attractive forces similar to those of water allowing contact between the individual water and oil molecules. The imbalance between the attractive forces of the water and oil molecules leads to an imbalance of forces at the interface. This is corrected by the contraction of one fluid and the expansion of the other until the forces are balanced. Usually the fluid with the stronger intermolecular attraction will contract, and reduce the area of the interface. The surface energy in each fluid required to form the interface is called the interfacial tension. Antanouv's rule (Equation 2-1) states that interfacial tension is equal to the differences between the surface tensions of the fluids. (Surface tension is equivalent to the fluid-air interfacial tension).

$$\Gamma_{ow} = \Gamma_{aw} - \Gamma_{ao} \quad 2-1$$

where:

- Γ_{ow} = interfacial tension between oil and water, dyne/cm,
- Γ_{aw} = surface tension between air and water, dyne/cm, and
- Γ_{ao} = surface tension between air and oil, dyne/cm.

Since the interaction between the two liquid phases takes place on the surface of the rock, the forces between the fluids and the rock (adhesion) must also be considered.

Dupre's equation describes the interaction between the fluid and the solid terms of their interfacial tensions.

$$W_a = \Gamma_{sa} + \Gamma_{la} - \Gamma_{sl} \quad 2-2$$

where:

- W_a = the work of adhesion, erg/cm^2 ,
- Γ_{sa} = interfacial tension between solid and air, dyne/cm ,
- Γ_{la} = interfacial tension between liquid and air, dyne/cm , and
- Γ_{sl} = interfacial tension between solid and liquid, dyne/cm .

Young developed a more practical equation which describes the work of adhesion in terms of liquid-air interfacial tension and the contact angle.

$$W_a = \Gamma(1 + \cos \theta) \quad 2-3$$

where:

- W_a = the work of adhesion, erg/cm^2 ,
- θ = contact angle, and
- Γ = surface tension of the liquid, dyne/cm .

The contact angle is the angle of intersection between the two fluids at the rock surface, measured through the denser phase. (See Figure 2-1). Thus, by measuring the surface tension of the fluids and the contact angle, a value for the work of adhesion can be obtained. By combining the interfacial forces between the oil and the water with the oil-rock and water-rock work of adhesion, an equilibrium or summation of the forces at the interface is obtained.

Generally, wetting is defined as the phenomenon that occurs when a solid and a liquid phase come in contact in such a manner as to form a solid-liquid interface. In reservoir engineering, "wetting" or "preferential wetting" is used to describe the property of the rock that allows the wetting fluid to spread over the rock surface in the presence of another fluid. Reservoir rocks are considered either oil-wet, water-wet or intermediately wet.

Wettability is dependent upon the surface forces, the adhesion and the interfacial tensions. For water to displace oil from the surface of the rock Adam¹ shows $W_{aw} - \Gamma_{wa}$ must be greater than $W_{as} - \Gamma_{oa}$, whereas for oil to displace water, $W_a - \Gamma_{oa}$ must be greater than $W_{aw} - \Gamma_{wa}$. An ideal wetting fluid would be characterized by a small contact angle, have high adhesion to rock, and a low

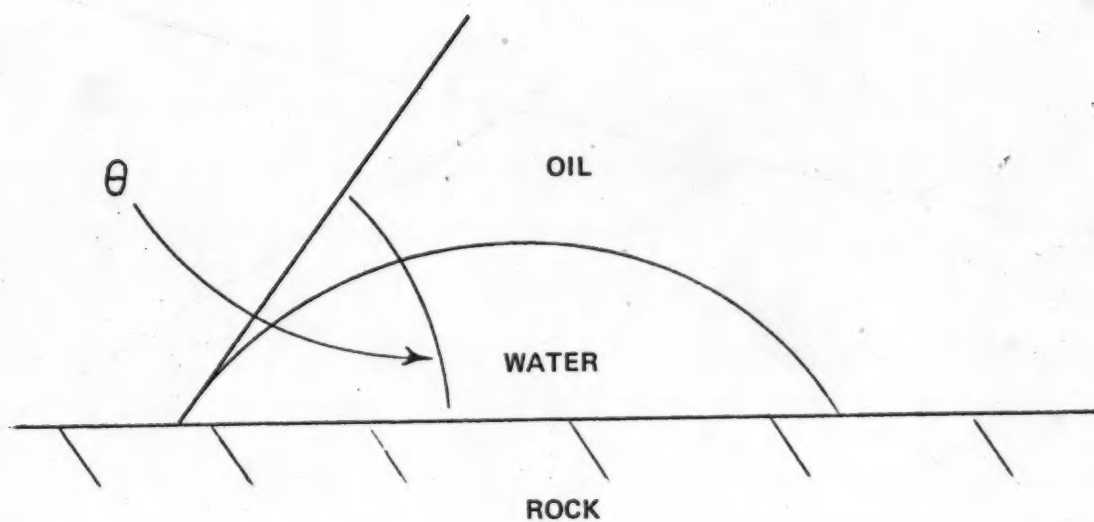


FIGURE 2-1 SCHEMATIC REPRESENTATION OF A CONTACT ANGLE FOR A ROCK, WATER, OIL SYSTEM

interfacial tension with the other fluid.

A surfactant is a surface active chemical which concentrates at an interface and upsets the equilibrium of the interfacial forces. The surfactant molecule is highly symmetrical, one portion being polar and the other, non-polar. In an oil-water system, the polar section is attracted by the polar water molecules, while the non-polar section is attracted by the non-polar oil. Thus, the surfactant molecule migrates to the oil-water interface (Gibb's rule of solution concentration at an interface) and positions itself so that its polar section is in the water, while the non-polar section is in the oil. This surfactant film lowers the amount of energy required to maintain the interface, thereby reducing interfacial tension.

The removal of oil from the surface by the use of a surfactant occurs in one or both of two mechanisms:

1. Solubilization
2. Surface Roll-up

Solubilization is the process by which the oil molecules are surrounded by the surfactant, forming micelles in the aqueous phase. A micelle is a structure formed by an oil molecule surrounded by surfactant molecules in such a way that the non-polar portion of the surfactant is towards the oil and the polar portion is towards the

water. This allows the oil molecule to be removed into the aqueous phase.

Surface roll-up is a mechanism where the surfactant is adsorbed by the solid surface and forms a monolayer upon it. This reduces the surface tension of the aqueous phase, and the amount of water required to adhere to the surface. To balance this reduction in surface forces, the contact angle must also become less. If the surface tension and work of adhesion of the aqueous phase is lowered enough, the aqueous phase will displace the oil from the surface.

In general, adsorption is the physical and chemical process by which one phase interacts on a molecular scale with another phase, to reduce the energy of their interface. In this study, only the highly specific adsorption between a solid or liquid and a solution will be discussed. Irreversible adsorption occurs when a component of one phase reacts with a component of the other phase to form a reaction product at the interface.

Reversible adsorption occurs when surface energy at an interface is lowered by the attraction of a high concentration of solute molecules to the surface of the solution. Gibbs²⁴ showed that an increase in solute concentration at the interface must occur to reduce the

surface to its lowest energy state. The presence of the solute molecules causes a disruption of the bonding between the solvent molecules. Adsorption of the solute on the interface is dependent upon the chemical and physical structures of the solute, solvent, and adsorbent. When the two phases are similar, the interface is at a low energy level and requires little adsorption to lower it further. Highly dissimilar phases result in a high degree of adsorption, because of their high energy interfaces. The most effective tension-lowering solutes are the previously mentioned surfactants.

EXPERIMENTAL EQUIPMENT

The displacement and saturating apparatus schematically diagrammed in Figure 3-1 consists of three separate sections:

1. The displacement apparatus.
2. The saturating apparatus.
3. The injection cylinder panel.

The cylinder panel consists of six 3000 cc high-pressure stainless steel cylinders connected such that mercury could be injected into the bottom of the cylinders displacing the stored fluid into either the displacing or the saturating apparatus. By isolating one-half of the panel from the other, it was possible to saturate one core while conducting displacement tests on the other core. Due to the high viscosity of Lloydminster crude, it was necessary to use a hydraulic pump to inject it into the oil storage cylinder. All lines through which oil was passed were 1/4 inch stainless steel tubing; all other lines were 1/8 inch stainless steel tubing.

The saturating apparatus consists of a core holder with pressure taps mounted at the upstream and downstream ends. Both a manometer and a differential

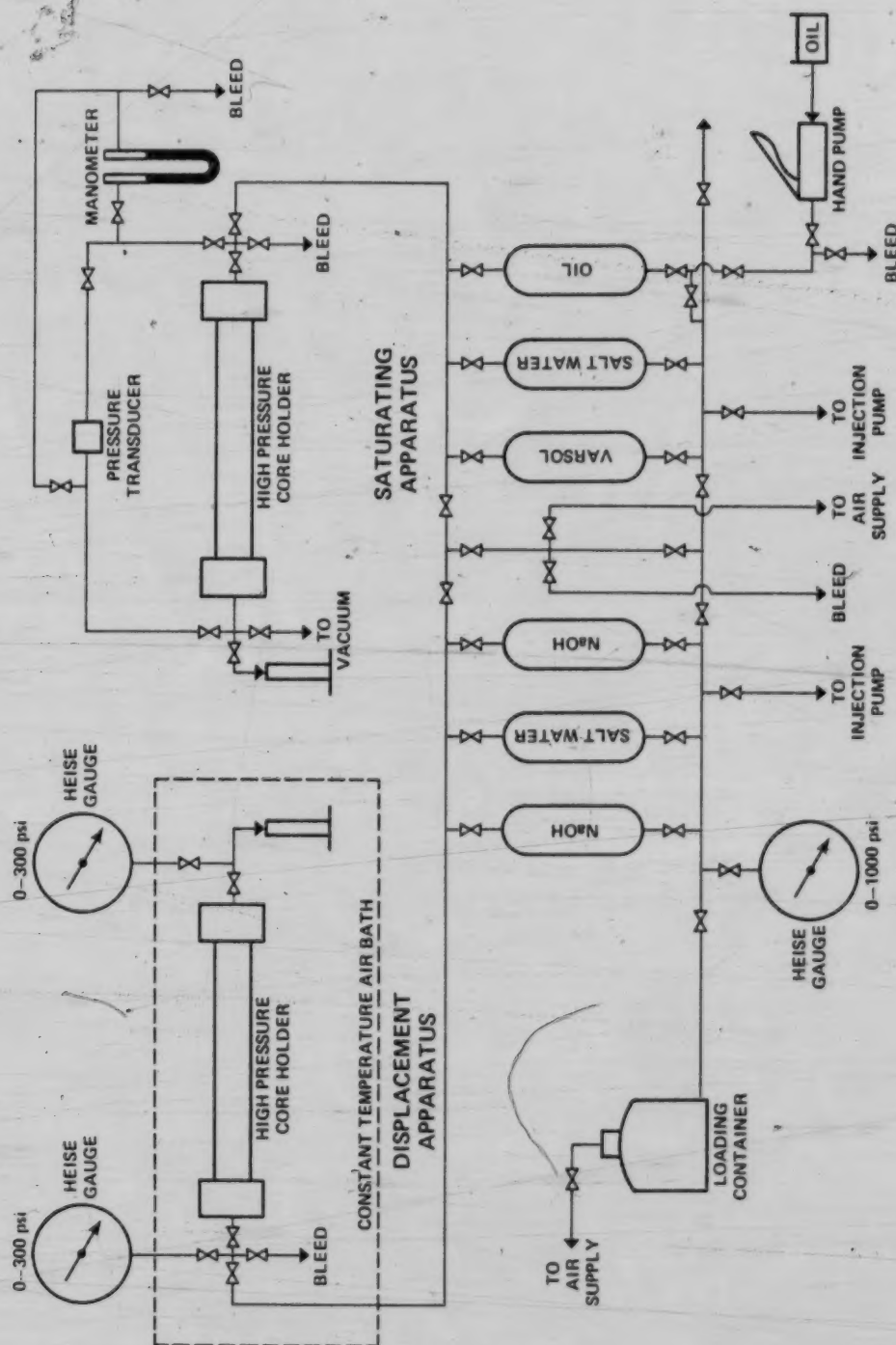


FIGURE 3-1 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL EQUIPMENT

pressure transducer were used to measure differential pressure. A Validyne pressure transducer, with an accuracy of ± 0.025 psi over a range of 5 psi was used. It was bridged with a Validyne model CD15 potentiometer and read-out on an Advance Digital multimeter. Prior to each core saturation the transducer was calibrated with the manometer. A vacuum pump, connected to the downstream end of the core holder, was used to evacuate the core prior to saturation. The "Displacement" apparatus consists of the core holder with pressure taps mounted at the upstream and downstream ends. Pressure taps were connected to calibrated Heise gauges to measure the upstream and downstream pressures. The displacement apparatus was enclosed in a constant temperature air bath, thermostatically controlled to within $\pm 1.0^\circ$ F.

Two high-pressure stainless steel core holders were used. Each consisted of a stainless steel tube (97.47 cm long, 4.95 cm inside diameter) with two removable end plates. The end plates fitted over a 200 mesh stainless steel screen which prevented movement of the sand and plugging of the inlet or outlet lines. A Ruska, constant-rate, two-barrel, mercury-injected pump was used to inject mercury into the cylinders. The injection rate could be varied from 2.5 cc/hr to a maximum of 1120 cc/hr using both barrels. The effluent

from the saturating and displacement runs was collected in 50 cc centrifuge tubes. An International centrifuge was used to break the emulsions produced. The viscosity measurements were taken with a Cannon-Fenske viscometer (for opaque liquids) in a constant-temperature water bath. Wettability measurements were conducted with apparatus similar to that described by Bobek, Mattax, and Denekas⁶. A Lucite cell (2-inch long, 1-inch inside diameter) was used to hold the unconsolidated sand pack. A Cenco du Noüy tensiometer with a platinum ring 6 cm in circumference was used for all interfacial tension measurements. All tests at elevated temperatures were conducted in the constant temperature air bath. A Rediameter Titrator pH meter with glass electrodes was used for all pH readings. The pH meter was calibrated with a buffer solution standard after each measurement.

EXPERIMENTAL PROCEDURE

Source and Handling of Materials

Two types of sand were used in this study. A Golpher sand for the 1000 series runs to establish model scaling properties and a natural Sparky sand from the Lloydminster Area for all other runs.

The Sparky sand used was obtained from a lease storage tank, having been produced along with the crude. The sand was washed with Varsol until no traces of oil were observed. It was then suspended upon a series of screens and N-Pentane was allowed to permeate through until all discoloration of the effluent N-Pentane disappeared. The sand was then dried in an oven for 5 to 12 hours at a temperature of 210° F. A considerable amount of large rust flakes were removed from the sand by passing the sand through a series of sieves. All sand particles smaller than 200 mesh were collected and removed before use.

The Golpher sand, a clean commercial sand, similar to Ottawa sand was used without alteration other than the sieve removal of particles smaller than 200 mesh.

Lloydminster crude oil treated only for removal

of water was used for all displacement tests presented in this study. An A.S.T.M. standard test for water in petroleum by distillation (A.S.T.M. designation D95-62) indicated that the oil contained 0.18 percent by volume BS&W. The crude oil gravity was found to be 16.1° API by the hydrometer method (A.S.T.M. designation D287-55). Viscosity of the crude oil was measured at several temperatures using a Cannon-Fenske viscometer for opaque liquids following the procedure outlined by A.S.T.M. test D4445-60. These properties are summarized in Appendix A.

An artificial brine was used in all the oil displacement tests. The brine consisted of 88.84 grams of sodium chloride per litre of distilled water. This was the same as the brine used by Scott⁴⁰ and Scott⁴¹. It was selected to match the chloride ion concentration of the natural field water. Reagent grade sodium chloride was used in all brine solutions. As it was pure, it did not affect the pH of the distilled water. Commercial grade salt when added to the distilled water changed the pH from 7.6 to 9.4. Since the pH of the effluent from displacement tests was monitored, the use of commercial salt would be impractical. (Displacement tests using commercial salt showed a marked increase in recovery over tests using reagent grade salt).

Core Packing

The core holder with the bottom end plate in position (200 mesh screen in place) was placed in a vertical position. Three electric vibrators were strapped in place, one at the top, one at the base and one at the center of the core holder. The core holder was then filled half-full of water and the vibrators turned on. The dry sand was poured into the core holder through a funnel which regulated the input to approximately 50 cc per minute until it became full. The water level was kept above the sand level in the core holder at all times. Once the core holder was full, it was tapped repeatedly using a small hammer until the sand ceased to compact. The core holder was then filled to the top with sand and the other end plate (with 200 mesh screen) attached. With the vibrators operating, water was run through the core until no more compaction occurred. At each inspection for compaction the core was tapped and filled to the top with sand. When no more compaction occurred, dry air was passed through the core for 8 to 12 hours to remove the water. The core holder, full of dry sand, was then ready for the displacement test. Silica grease was used on the end plate threads to prevent any fluid loss. The end plates were tightened until the core holder was the same length for all runs.

Measurement of Core Properties

The porosity of the sand packs were measured by the material balance method. Vacuum was drawn on the core by the pump connected to the outlet end. Brine was then injected and the injection pressure monitored until an increase was observed. The outlet end of the core holder was opened and the effluent brine collected in a graduated cylinder. Brine was flowed through the core until steady state flow conditions occurred. The pore volume of the core was taken to be the difference between the amount of brine injected and the amount of brine produced from the downstream end. Knowing the volume of the core holder, the porosity was calculated.

The absolute permeability of the sand pack was obtained by flowing brine through the core at several constant rates and measuring the differential pressure across the core. Darcy's linear flow equation was used to calculate the permeability.

After the permeability was measured, the crude oil was injected into the core and the effluent brine was measured in graduated cylinders. After breakthrough of the oil, the effluent was collected in centrifuge tubes, heated and centrifuged to break the oil water emulsion. When all traces of water disappeared from

the effluent stream, the core was ready for the displacement test. Initial water saturations and initial oil in place were obtained by maintaining a material balance on the core during the whole procedure.

Displacement Test Procedure

After saturation and measurement of initial properties, the sand pack was placed in the constant temperature air bath and allowed to acclimatize for 8 to 12 hours. The displacement test was then run and the produced effluent was collected in 50 ml centrifuge tubes. The differential pressure across the core at the end of each sampling was tabulated along with the total volume of the effluent sample. The sample was heated and centrifuged to break the oil water emulsion, and the oil and water volumes were tabulated. For displacement tests requiring pH measurements, the effluent water, after separation, was pipetted into a 50 ml beaker and measured.

Core Handling

Five 1000 series displacement runs were made on the same Golpher sand pack. At the conclusion of each run, the core was displaced to its residual water saturation by running crude oil through until there was

no trace of water in the effluent. Runs 2003 and 2004 were run on the same Sparky sand pack, using the same resaturation technique. All other runs were made on fresh sand packs.

Interfacial Tension Measurement Procedure

Interfacial and surface tensions were measured using a Du Noüy ring tensiometer. The procedure outlined by A.S.T.M. test D971-50 was followed throughout. All surface tensions were measured at room temperature (76°F). All crude oil and sodium hydroxide solution interfacial tensions were measured at 87°F in the air bath. Accurate measurement of tension values less than 0.5 dyne/cm were impossible due to the high viscosity of the oil. (Unable to observe an exact break point.)

Wettability Measurement Procedure

Two methods of measuring wettability were used.

1. A bench test.
2. The cell imbibition test.

The bench test consists of placing a drop of fluid on a dry surface and observing the rate of movement into the

sand surface and observing the rate of movement into the sand with a magnifying glass. If the fluid moved quickly into the sand, the sand was said to be wetted by that fluid. This test procedure gives a highly qualitative measurement of wettability.

The cell imbibition tests followed procedures described by Bobek, Mattax, and Denekas⁶. A small lucite imbibition cell was packed with sand by vibrating the cell until the sand ceased to compact. The end plate with a 200 mesh screen was then fastened on, and the packed cell weighted. The cell was saturated by evacuating it in a vacuum cell, which was then filled with saturating fluid until the imbibition cell was immersed. The imbibition cell was then re-weighed to obtain the porosity of the sand pack by weight difference. The saturated cell was then placed in the imbibition column which was filled to the graduated portion of the column, completely immersing the imbibition cell with imbibing fluid. The saturating fluid displaced by the imbibing fluid was collected and measured in the graduated portion of the column. The measured displaced fluid was then tabulated along with imbibition time. All tests were run at room temperature.

MODEL SCALING

The use of laboratory models to predict performance of actual reservoirs requires that the physical properties of the models are scaled. If the models are properly scaled, viscous fingering and capillary end effects can be minimized or eliminated. Investigation of these scaling problems has resulted in the development of scaling groups by several authors.

Rapoport and Leas³⁸ used the following scaling factor to study capillary end effects.

$$LV\mu_w$$

5-1

where: L = length of the core, cm,
 V = velocity (flow rate/cross-sectional area), cm/min, and
 μ_w = injection water viscosity, cp.

They found that for values greater than 1.0, recovery did not change with changes in magnitude of the scaling factor. This would indicate that for systems having scaling factors greater than 1.0, capillary end effects are negligible. de Haan¹³ elaborated on the Rapoport and Leas' factor to account for interfacial tension and permeability. de Haan¹³ proposed the following scaling factor.

$$I = \frac{V\mu_w L}{\gamma\sqrt{K}} \quad 5-2$$

where: I = de Haan scaling coefficient,
 V = velocity (flowrate/cross-sectional area), cm/sec,
 μ_w = viscosity of the injected water, cp,
 L = length of core, cm,
 γ = interfacial tension, dyne/cm, and
 K = absolute permeability, md.

He stated that for oil-wet or neutral systems there would be no viscous fingering for scaling coefficient values less than 0.1. (The advance of one portion of the flood front ahead of the rest of the front in a homogeneous media due to viscosity differences between the displaced and the displacing fluid is called viscous fingering).

Chuoque, van Meurs and van der Poel⁸ also developed a scaling factor to test for viscous fingering.

$$\frac{\lambda_{cr}}{h} = C \frac{3\sigma_{wo} K}{V(\mu_o - \mu_w)} \quad 5-3$$

where:

- λ_{cr} = critical fingering distance, cm,
- C = dimensionless, experimental constant,
- σ_{wo} = interfacial tension, dyne/cm
- V = velocity, (flowrate/cross-section area), cm/sec,
- K = absolute permeability, cm^2 ,
- μ_o = oil viscosity, poise,
- μ_w = water viscosity, poise, and
- h = lateral dimension of core, cm.

They showed that for scaling factor values greater than 1.0 fingering did not occur since the mean thicknesses of the fingers were larger than the diameter of the core. For a scaling factor in the region of 1.0, prolific viscous fingering occurs. If the scaling factor values are much less than 1.0 minute fingers occur with a mean thickness so small that the recoveries are insensitive to fingering. As illustrated in Figure 5-1 recovery is sensitive to changes in the scaling factor for scaling values approaching 1.0. Recovery changes little when the scaling factor is much greater or much less than 1.0.

For the core system used in this study a series of displacement tests at different injection rates were

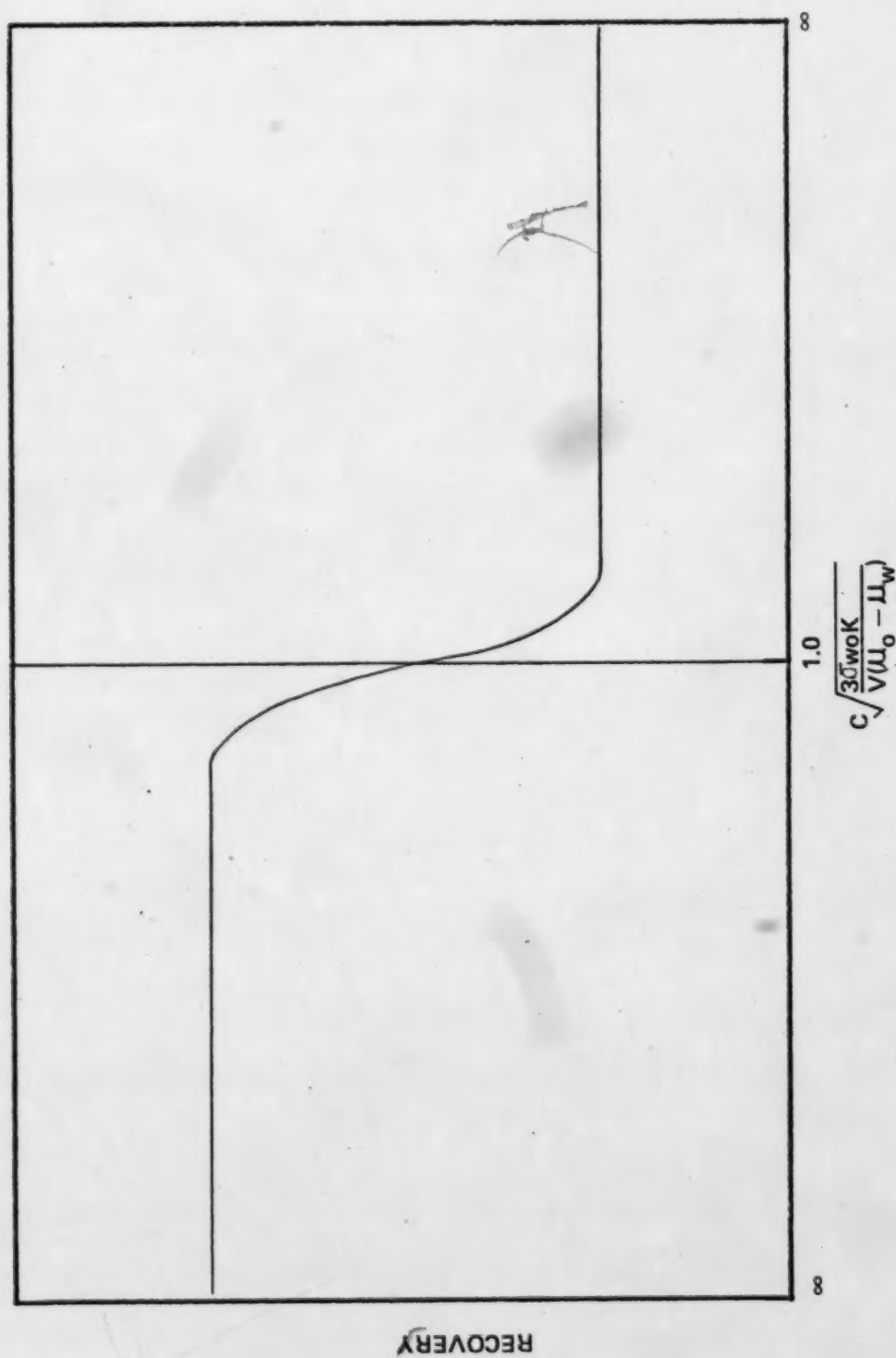


FIGURE 5-1 IDEALIZED DIAGRAM OF RECOVERY AS A FUNCTION OF CHUOKE ET AL. SCALING COEFFICIENT

run. A summary of displacement test initial properties and recoveries is presented in Table B-1. Also included in Table B-1 are the values of the Rapoport and Leas, de Haan, and Chuoke et al. scaling coefficients for the core system at each rate.

The Rapoport and Leas scaling coefficient was plotted as a function of the injection rates used in this study (Figure 5-2). A rate greater than 11.5 cc/hr was required to negate capillary end effects. (A rate greater than 11.5 cc/hr is required to produce a scaling factor value greater than 1.0).

The de Haan and Chuoke et al. scaling coefficients were plotted as a function of recovery in Figures 5-3 and 5-4 respectively. To obtain the Chuoke et al. coefficient a value of 250 was used as the dimensionless coefficient. This value was suggested by Collins⁹ for viscous crude systems with initial water saturations.

Except for a small decrease in the breakthrough recovery versus the Chuoke et al. coefficient and a small increase in the breakthrough recovery versus the de Haan coefficient, recovery showed no sensitivity to the magnitude of either scaling coefficient. The differences between the breakthrough curves were attributed to experimental error. It was difficult to obtain a precise breakthrough due to the severe emulsification of the water in the oil.

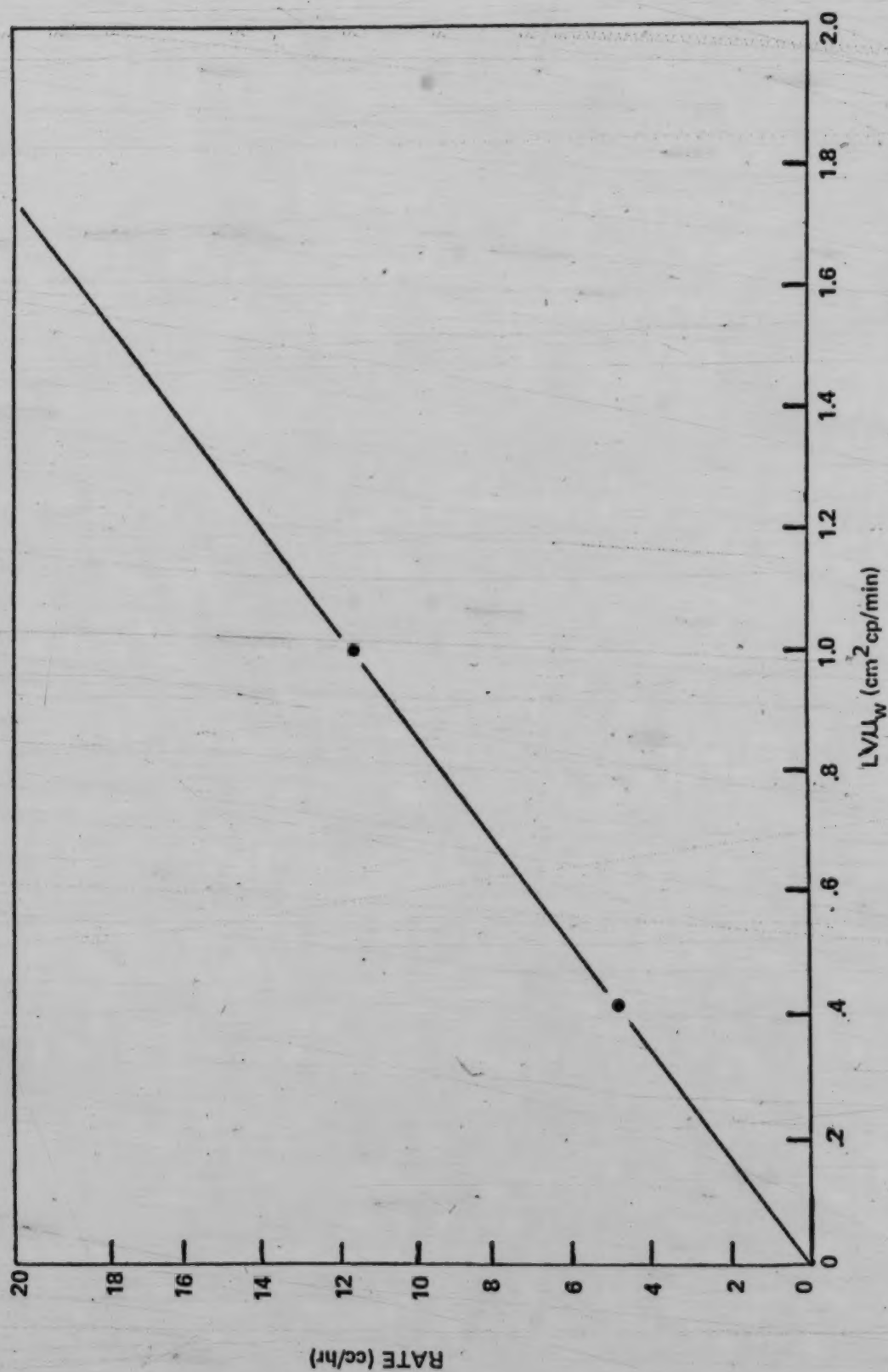


FIGURE 5-2 RAPOPORT AND LEAS SCALING COEFFICIENT FOR THE 97.47 cm BY 4.95 cm SAND PACK

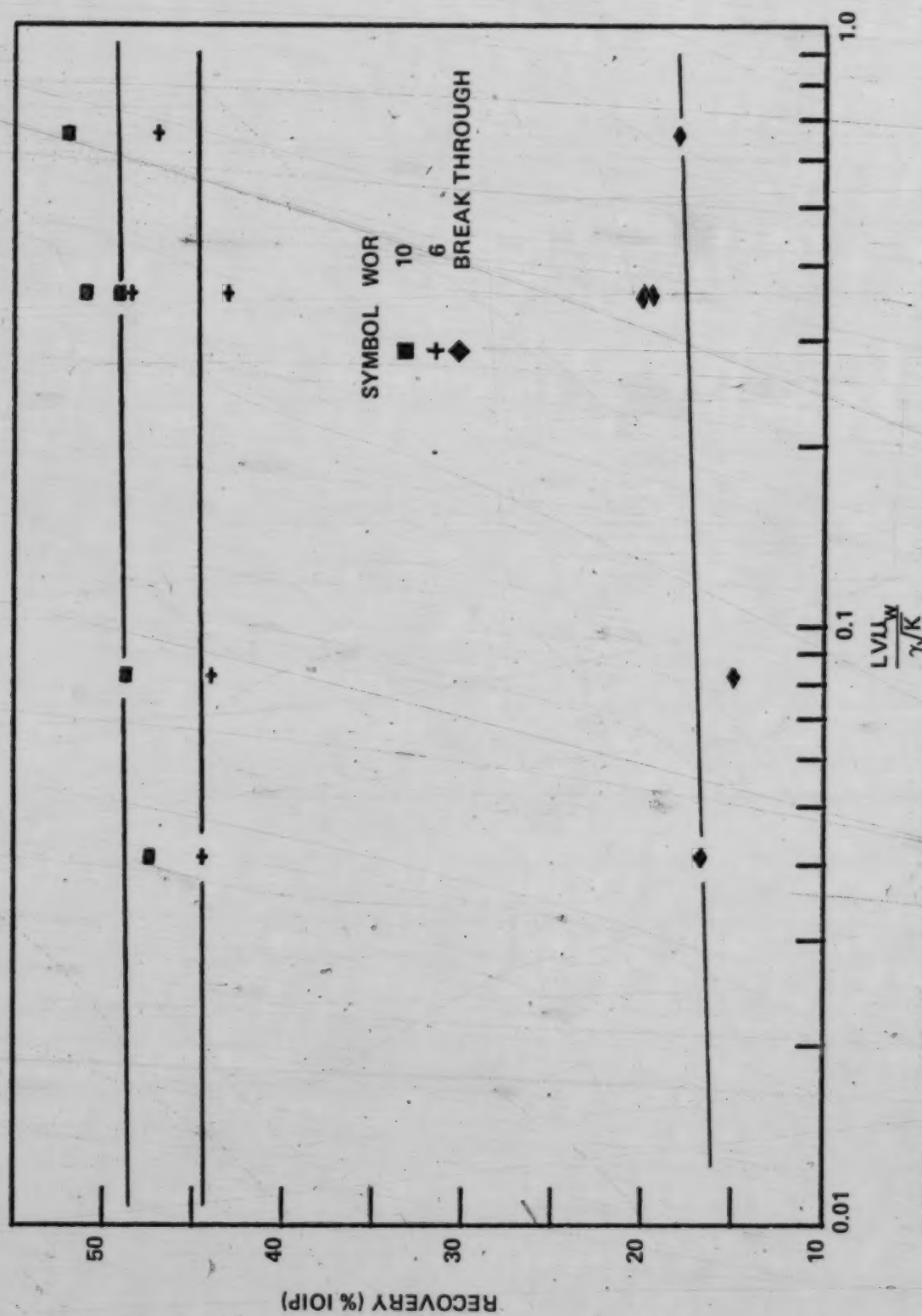


FIGURE 5-3 DE HAAN SCALING COEFFICIENT FOR THE 97.47 cm BY 4.95 cm SAND PACK

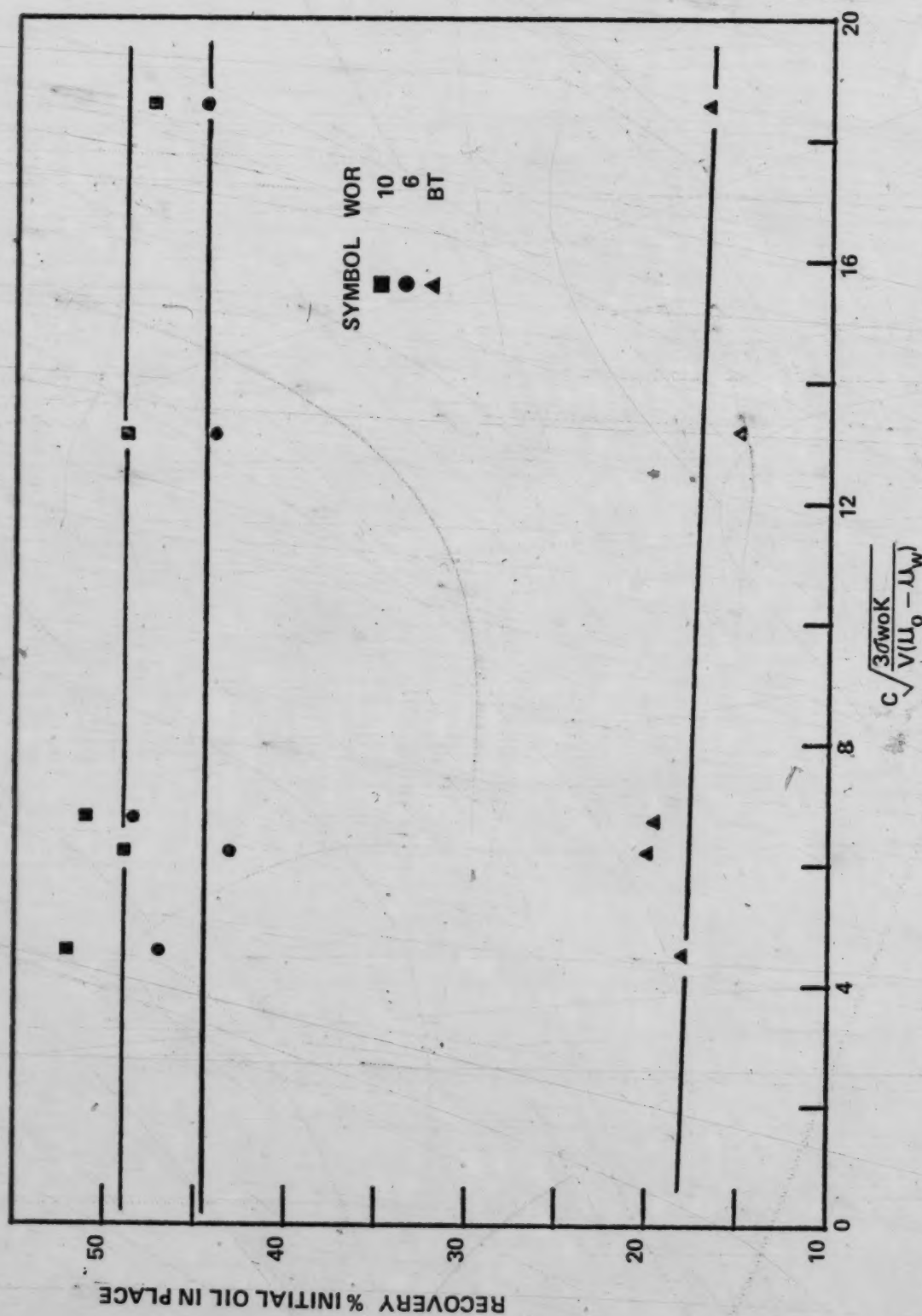


FIGURE 5-4 CHUOKE ET AL SCALING COEFFICIENT FOR THE 97.47 cm BY 4.95 cm SAND PACK

Recovery showed no sensitivity to rate as exhibited by Figure 5-5. This lack of sensitivity of recovery to rate would indicate that there is little or no viscous fingering at injection rates from 60 cc/hr to 960 cc/hr for this system.

As a result of the above investigation a rate of 320 cc/hr was selected for all further displacement tests. This rate was high enough to satisfy Rapoport and Leas' requirement to eliminate capillary end effects ($LV\mu_w = 20.45 \text{ cm}^2 \text{ cp/min}$). The de Haan coefficient for the system at 320 cc/hr was 0.22. This is slightly larger than the critical value 0.1 and introduces the possibility of viscous fingering according to de Haan. However, the value of the Chuoke et al. coefficient for this rate was 8.0 which implies no viscous fingering.

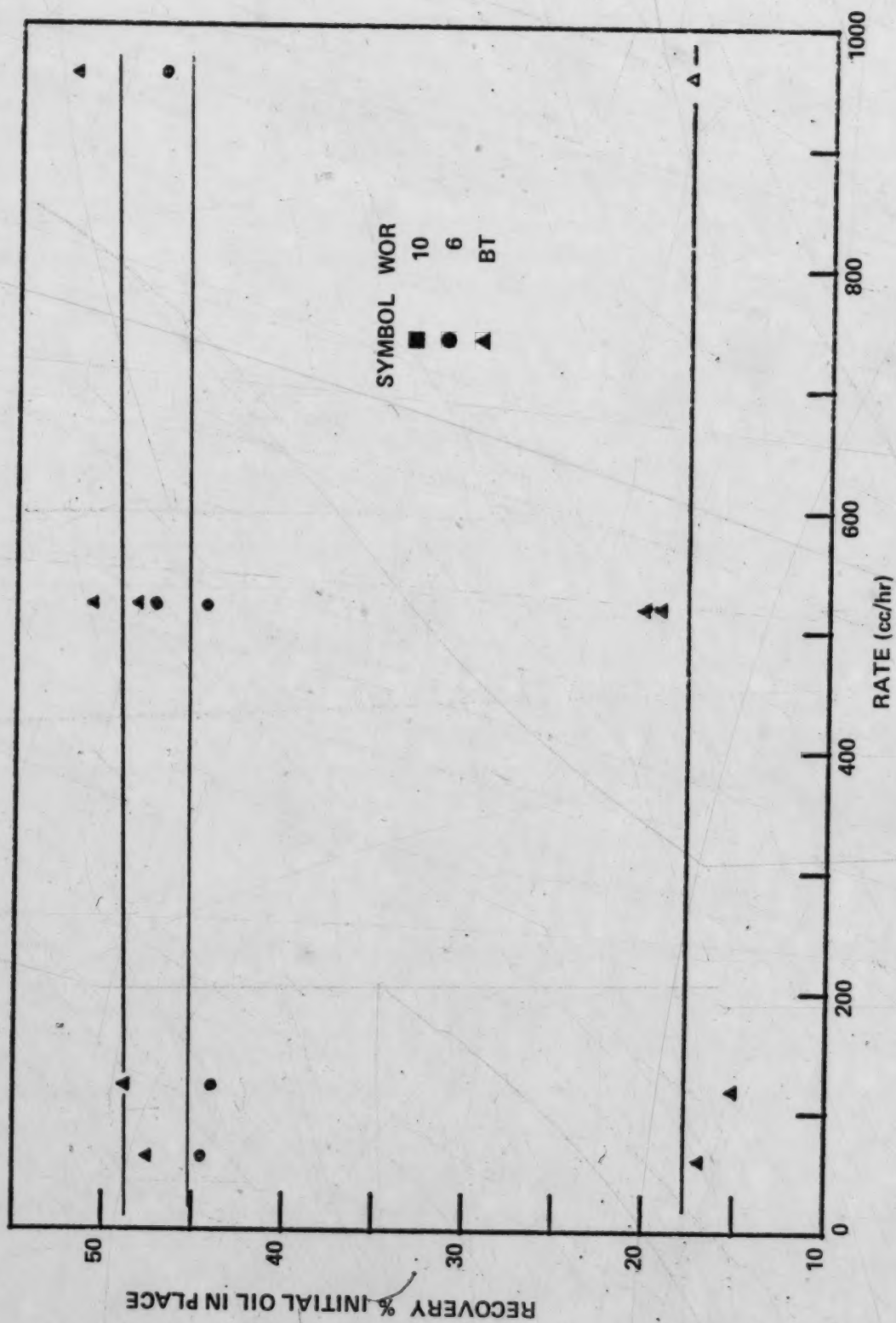


FIGURE 5-5 SENSITIVITY OF RECOVERY TO FLUID INJECTION RATE

EXPERIMENTAL RESULTS

Sand and Fluid Properties

The Golpher sand used in this study was a clean, coarse grained commercial sand. Its particle size distribution is presented in Figure A-1 and Table A-1. When packed, it formed an unconsolidated core with a porosity of 29 to 32 per cent and a permeability of 37 darcies.

The Sparky sand used was obtained from a lease tank, having been produced with the oil. This introduced the possibility that the Sparky sand had a higher concentration of finer grains and was not equivalent to the natural sand. A sieve analysis of the Sparky sand is presented in Figure A-2 and Table A-2. The particle size distribution shows a much higher percentage of finer grained sand than the natural Sparky sand distribution presented by Scott⁴¹. Unconsolidated sand packs formed using Sparky sand have porosities of 39 to 43 percent and permeabilities of 21 to 28 darcies.

The properties of the Lloydminster crude used are presented in Table A-3. Viscosity and density as a function of temperature are presented in Figures A-3 and A-4 respectively. The Lloydminster crude oil had

an API gravity of 16.1 degrees and contained 0.18 percent bottom sediments and water.

An artificial brine was used in all displacement tests. It had viscosities of 0.75 centipoise, 0.81 centipoise and 0.99 centipoise at 105°F, 83°F, 76°F respectively. An analysis of the natural brine is presented in Table A-4.

Interfacial Tension

Two sets of interfacial tension data were obtained.

1. Lloydminster Crude - Sodium Hydroxide in Brine
2. Lloydminster Crude - Air (surface tension)

The Lloydminster crude - sodium hydroxide in brine interfacial tensions are presented in Table A-5 and Figure 6-1 as a function of sodium hydroxide concentration. The addition of sodium hydroxide to the brine solution rapidly reduced the interfacial tension with the Lloydminster crude. Sodium hydroxide concentrations greater than 0.005 percent reduced the measured interfacial tension below 0.5 dyne/cm (the minimum measurement of the du Noüy tensiometer was 0.5 dyne/cm).

Lloydminster crude - sodium hydroxide in brine

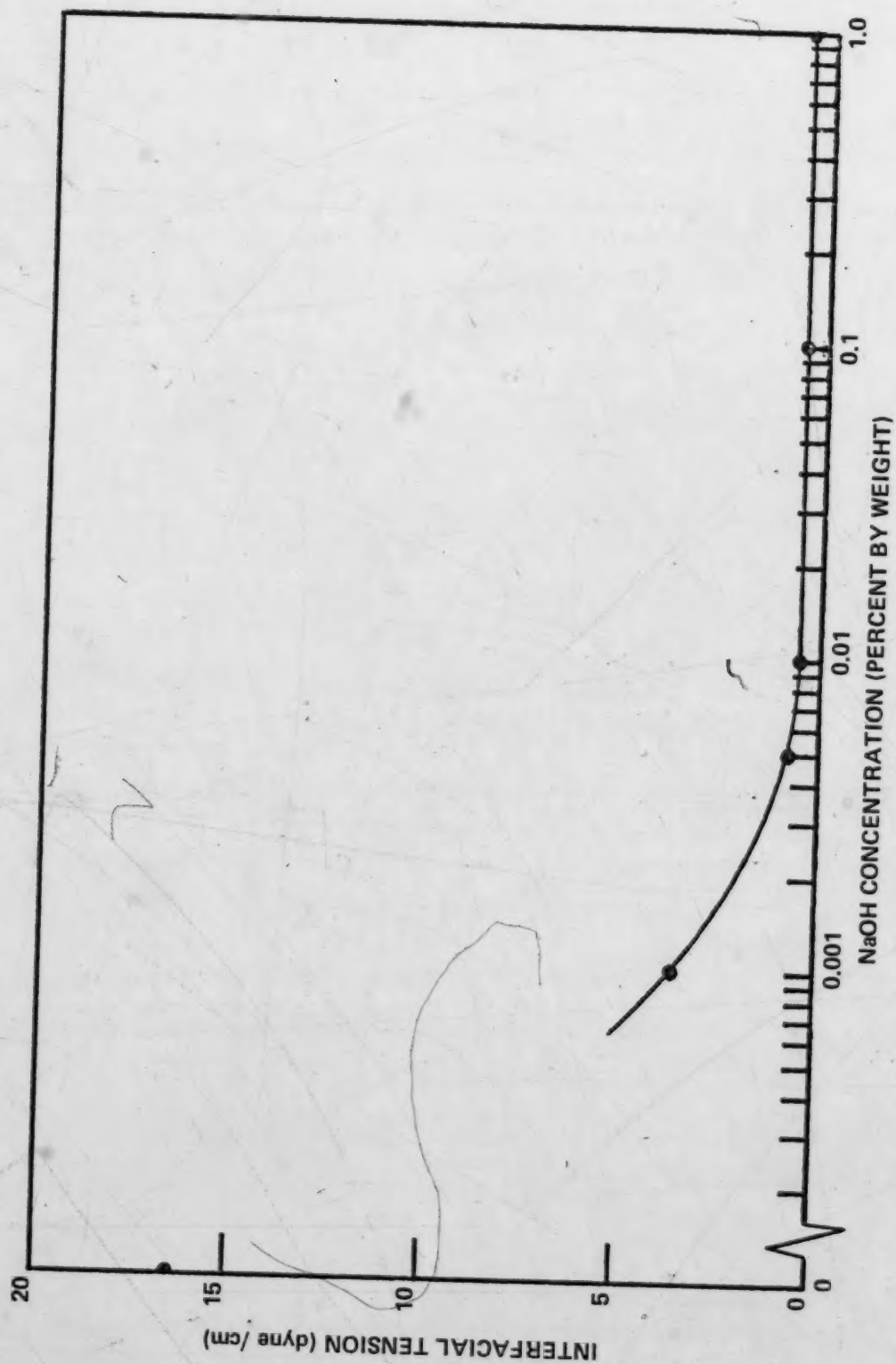


FIGURE 6-1 THE EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON THE INTERFACIAL TENSION OF LLOYDMINSTER CRUDE OIL

interfacial tension as a function of pH is presented in Figure A-5. This curve was obtained by cross plotting Figure 6-1 with Figure A-6, a plot of sodium hydroxide in brine concentration as a function of pH. At pH values greater than 10.9 the interfacial tension was reduced to a value below 0.5 dyne/cm.

Wettability Measurements

Bench tests were conducted on fresh Sparky sand and Sparky sand collected from a core that had been subjected to a sodium hydroxide displacement test. Brine, 0.1 percent by weight sodium hydroxide in brine and a 15 percent by volume Lloydminster crude in Varsol solution were used as the imbibing fluids.

Brine did not move into the fresh sand at all; the sodium hydroxide brine solution did not move into the sand any significant amount; however, the crude-Varsol solution readily saturated fresh sand. This would indicate that the fresh Sparky sand as cleaned in this study was preferentially oil-wet.

The brine solution slowly moved into the sodium hydroxide flooded sand; the sodium hydroxide solution moved into the sand at approximately the same rate as the brine; the crude-Varsol solution moved into the

treated sand but less rapidly than it moved into the fresh sand. This would indicate the sand had been made less oil-wet or possibly neutral by the sodium hydroxide displacement test.

Imbibition tests were conducted on both fresh Sparky sand and sand that had been flooded with sodium hydroxide. Brine and 0.1 percent by weight sodium hydroxide in brine solution were used as the imbibing fluid. A 15 percent Lloydminster crude in Varsol solution was used as a saturating solution. An attempt was made to use natural Lloydminster crude as a saturating fluid but no imbibition occurred, probably due to the high viscosity of the crude.

Results of the imbibition tests are presented in Figure 6-2 and Table A-6. Brine would not imbibe into either the fresh Sparky sand or the sodium hydroxide treated sand. The 0.1 percent by weight sodium hydroxide in brine solution imbibed into both fresh and treated Sparky sand. More oil was displaced from the sodium hydroxide treated sand than from the fresh sand. Both brine curves are similar with most of the imbibition occurring in the first thirty minutes of the test.

The results of the bench tests and imbibition tests conducted would indicate that the fresh Sparky sand was preferentially oil-wet and that contact with

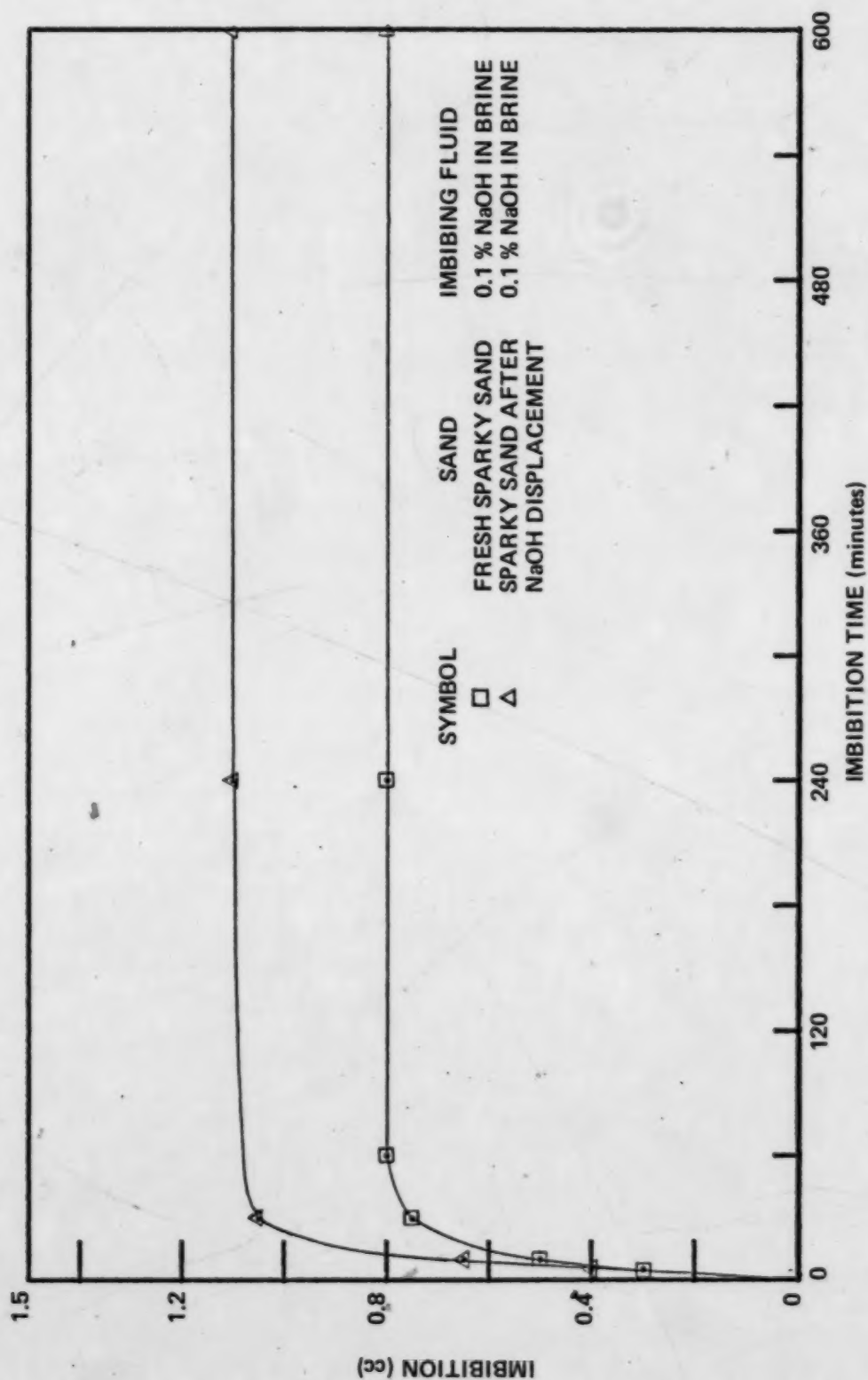


FIGURE 6-2 THE EFFECT OF SODIUM HYDROXIDE ON THE IMBIBITION RATE OF SPARKY SAND

sodium hydroxide caused a change in wetting, possibly due to a reduction in interfacial tension.

Core Properties

A summary of the initial conditions of the core used in the displacement tests is presented in Table A-8.

Although it was believed that high values of porosity and permeability might have been due to poor packing of the cores, inspection of the cores after each displacement test indicated no compaction. A possible explanation is that the grain size was fairly uniform. This yields a very porous sand pack.

The use of the same core for several displacement tests without cleaning between runs resulted in an increase in the initial water saturation between successive runs. The initial water saturation increased from 7.07 percent in the 1001 run to 29.41 percent for the 1005 and final run on the Golpher sand pack. The same behaviour was observed when a Sparky sand core was flooded twice (runs 2003 and 2004). The first run had an initial water saturation of 7.1 percent, while the second run had an initial water saturation of 20.9 percent.

Relative permeability calculations were made

using the method outlined in Appendix E on the data from displacement tests 6, 8 and 9. Results are presented in Tables E-1 through E-3 and in Figure E-1. The significant shift in the relative permeability curves is observed between the first and the second runs on core 4 (runs 2003 and 2004). This shift was attributed to an increase in the initial water saturation.

All subsequent tests were conducted on fresh sand packs to obtain uniform initial core properties. This was also made necessary by the fact that sodium hydroxide used in some of the displacement tests might chemically react with the sand changing its properties.

Displacement Tests

A summary of the displacement tests is presented in Table C-1. The results of the individual tests are presented in Tables D-1 through D-19.

Displacement tests are divided into four series of runs:

1. The 1000 series, "scaling factor runs".
2. The 2000 series, "base condition runs".
3. The 3000 series, "sodium hydroxide base condition runs".
4. The 4000 series, "slug injection runs".

The scaling factor runs were used to obtain an injection rate at which capillary end effects and viscous fingering would not affect the displacement test results. As previously mentioned in the section on model scaling, recovery was found to be insensitive to rate for the range tested. An injection rate of 320 cc/hr was selected for all further tests. This rate was high enough not to be affected by capillary end effects and low enough to inhibit viscous fingering.

The 2000 series base condition runs consisted of four displacement tests conducted to obtain a base brine displacement test. All further displacement test data would be compared to this base test to evaluate the effect of sodium hydroxide concentration and adjustment of slug size. Runs 2001, 2002 and 2003 were all conducted at the same conditions and produced similar results. Recovery at water breakthrough ranged from 9.56 to 11.67 percent of the initial oil in place. At 0.5 pore volumes injected, recovery ranged from 20.3 to 26.0 percent of the initial oil in place. Run 2003 was selected as the base brine flood as it represented an average of this series of displacement tests.

Run 2004 was conducted to observe if the same increase of initial water saturation occurred in Sparky sand as that observed in Golpher sand when multiple

runs were conducted on the same core. Initial water saturation increased from 7.1 to 20.9 percent as previously mentioned in the section on core properties. Run 2004 was conducted at an injection rate of 480 cc/hr to observe if recovery in Sparky sand was rate sensitive. No significant differences in results were observed between the tests at 480 cc/hr and tests at 320 cc/hr.

The 3000 series sodium hydroxide base runs were conducted to obtain recovery data on displacement tests employing different concentrations of sodium hydroxide in brine as displacing fluid. Concentrations of 1.0, 0.1, and 0.005 percent by weight sodium hydroxide were used. The addition of sodium hydroxide to brine resulted in little or no improvement in recoveries for concentrations of 0.005 percent sodium hydroxide or less. For concentrations of 0.1 percent sodium hydroxide a 25.45 percent recovery at water breakthrough was observed, a 15 percent increase over that obtained during the base brine flood. At 0.5 pore volume injection recovery was 39.7 percent compared to 23.5 percent for the base brine flood. The use of 1.0 percent sodium hydroxide in brine solution resulted in no significant improvement in recovery compared to the 0.1 percent sodium hydroxide in brine flood. The effect of the use of sodium hydroxide in brine on recovery is illustrated by Figure 6.3. The

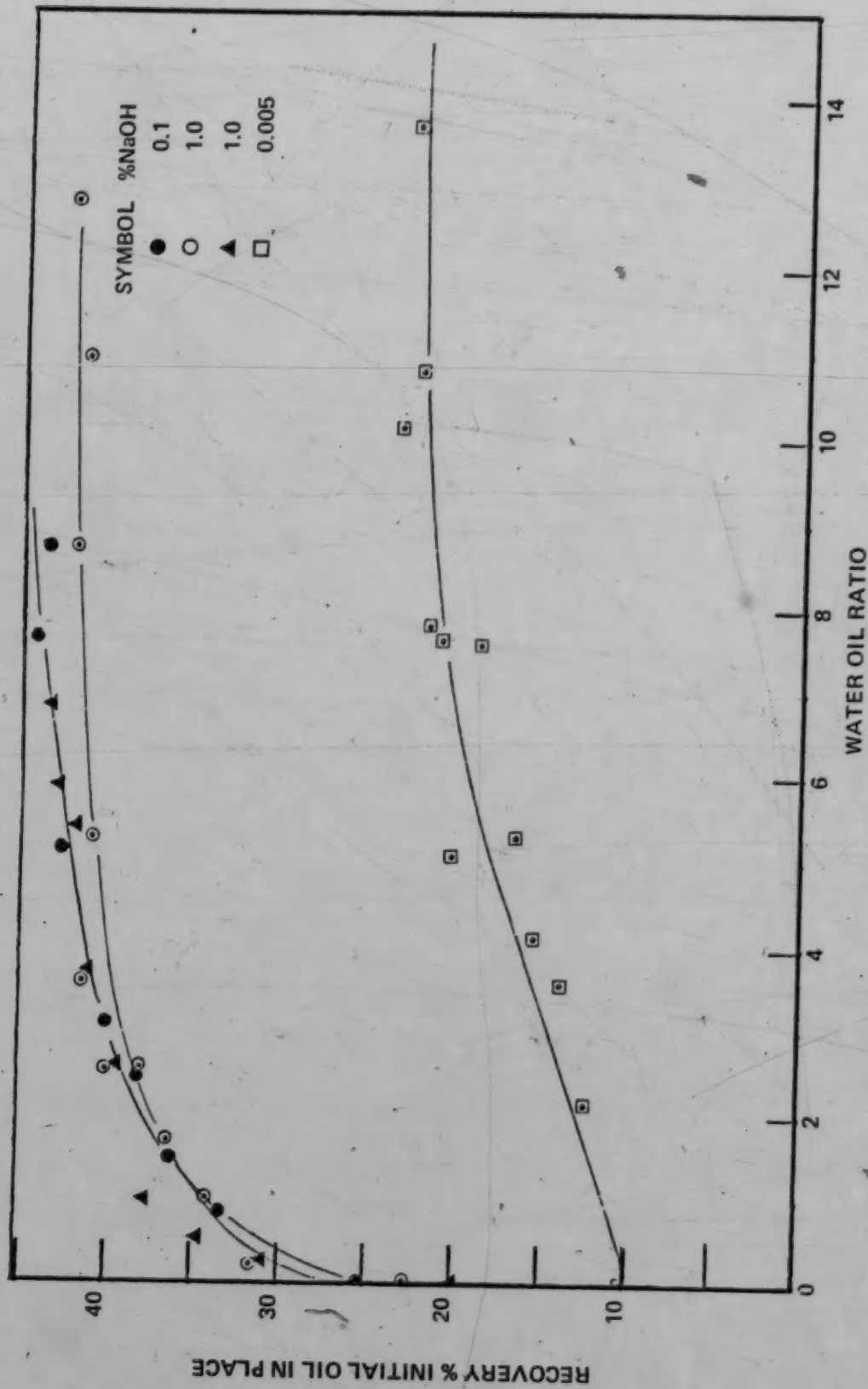


FIGURE 6-3 RECOVERY AS A FUNCTION OF WATER OIL RATIO FOR DIFFERENT SODIUM HYDROXIDE CONCENTRATIONS

majority of the increase due to sodium hydroxide, occurred prior to water breakthrough. A 9.0 percent breakthrough recovery was achieved with 0.005 percent sodium hydroxide as compared to 19.9 percent or 22.75 percent with 1.0 percent sodium hydroxide and 25.4 percent with 0.1 percent sodium hydroxide. The amount of subordinate recovery after a water-oil-ratio of 5 appears to be the same regardless of sodium hydroxide concentration.

Figure 6-4 illustrates that a minimum sodium hydroxide concentration of approximately 0.1 percent is required to give any significant increases in recovery. Increasing the sodium hydroxide concentration beyond 0.1 percent did not further increase recoveries. Scott⁴¹ obtained similar results flooding with sodium hydroxide in short cores.

Measurement of effluent pH during the displacement tests showed that the pH was slightly below the injection strength at water breakthrough; shortly after breakthrough the pH rapidly increased to injection strength.

The 4000 series slug injection runs were conducted to investigate the effect on recovery of adding sodium hydroxide to only a portion of the injected fluid. Five displacement tests were run using different slug sizes of 0.1 percent sodium hydroxide brine. The slugs

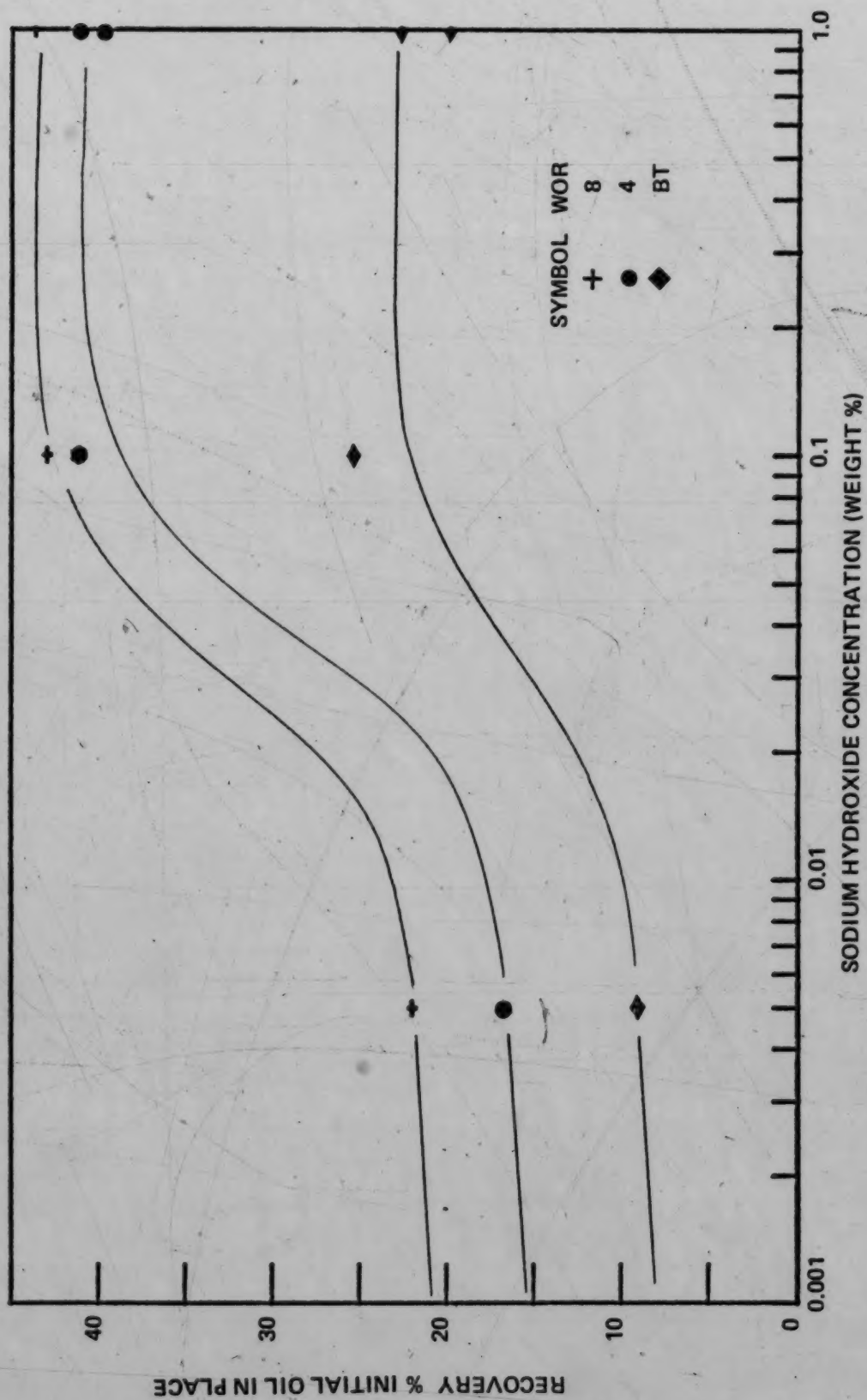


FIGURE 6-4 THE EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON RECOVERY OF LLOYDMINSTER CRUDE OIL

were pushed through the core by brine injected in the same manner as the sodium hydroxide slugs.

Figures 6-5 and D-1 illustrate the comparative recoveries of the different slug sizes used. Recovery tended to increase with slug size up to 325 cc (0.433 pore volume). The 325 cc (0.433 pore volume), 402 cc (0.536 pore volume), and infinite slug sizes seemed to produce identical recoveries. A cross plot of Figure D-1 presented as Figure 6-6 shows recovery as a function of slug size for three water oil ratios. The optimum slug size, or minimum slug size required to obtain maximum recovery, is approximately 300 cc (0.4 pore volume) for this core system using a sodium hydroxide slug concentration of 0.1 percent. Increasing the slug size above 300 cc (0.4 pore volume), as illustrated in Figure 6-6, did little to improve recovery.

The pH of the effluent was monitored for each different slug size (see Figures D-3 through D-7) and graphed in Figure 6-7. The profile of the pH curves are highly dependent upon slug size. The slugs of 105 cc (0.14 pore volume) and 250 cc (0.33 pore volume) had similar profiles with a rapid drop in pH after water breakthrough, approaching the pH of the brine (7.6). The 325 cc (0.433 pore volume) and 402 cc (0.536 pore volume) slugs had similar profiles, with pH increasing to injection strength (12.0) shortly after breakthrough,

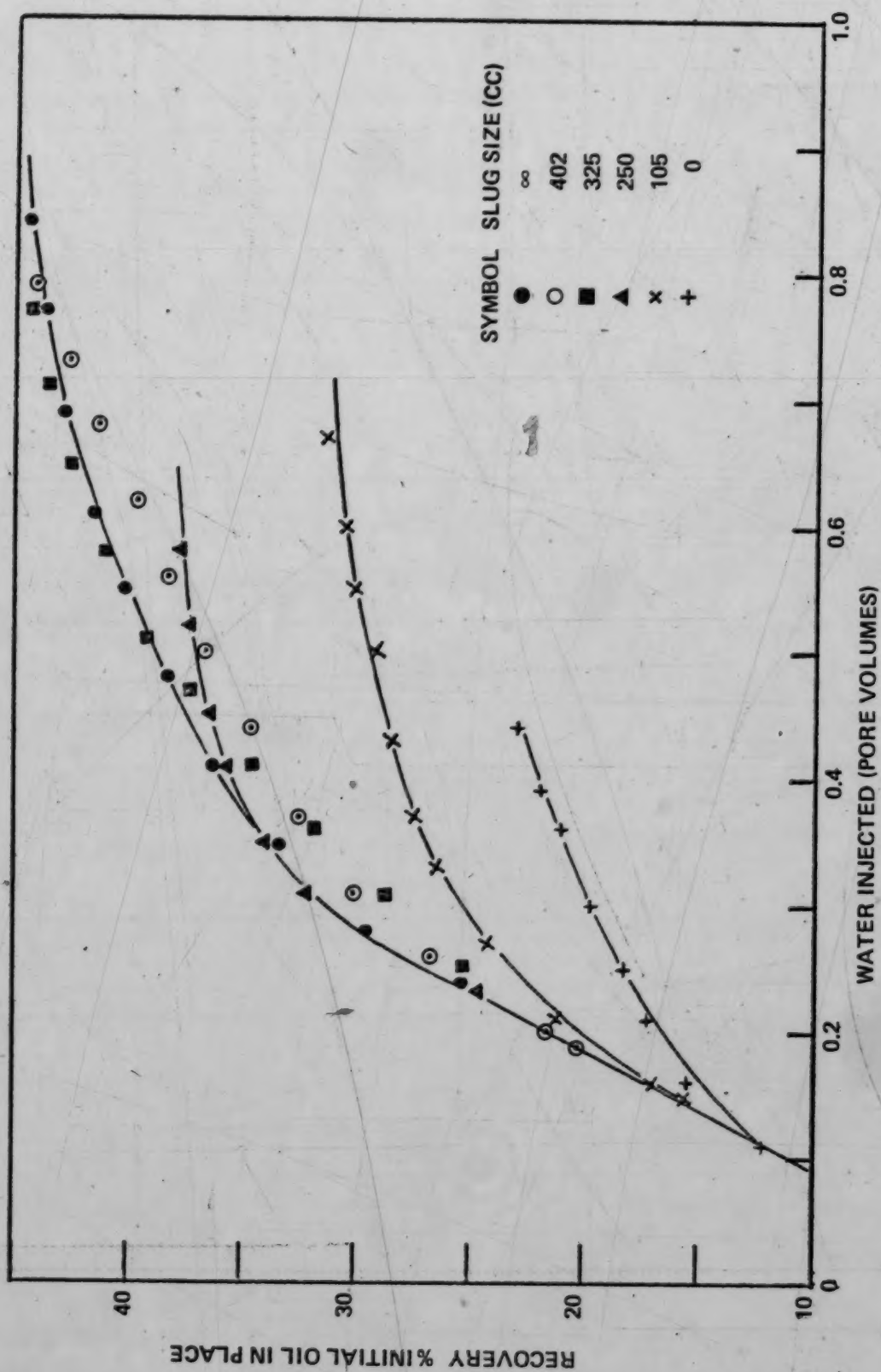


FIGURE 6-5 OIL RECOVERY USING DIFFERENT SLUG SIZES OF 0.1 PERCENT BY WEIGHT SODIUM HYDROXIDE

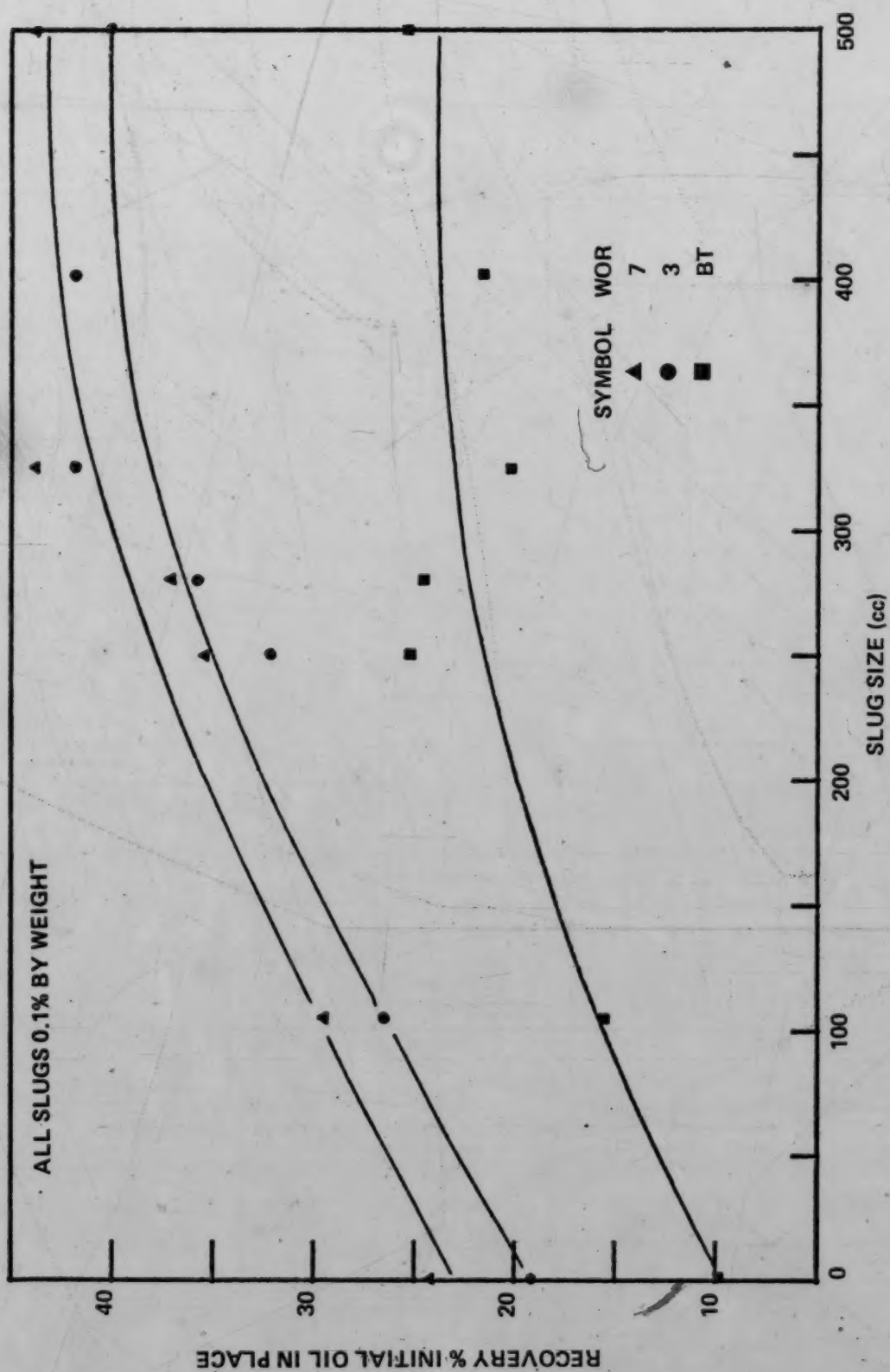


FIGURE 6-6 THE EFFECT ON RECOVERY OF USING 0.1 PERCENT BY WEIGHT SODIUM HYDROXIDE SLUGS

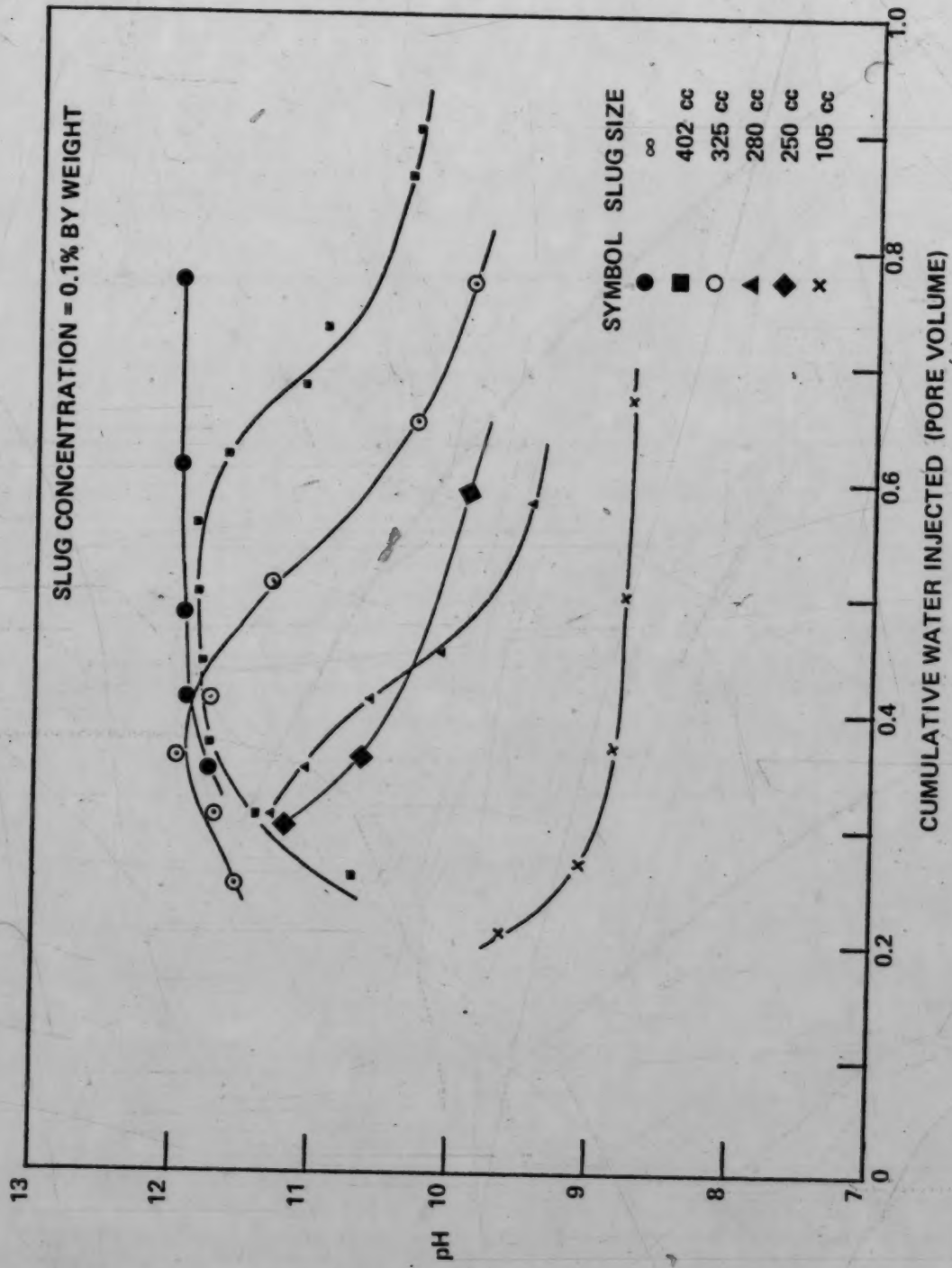


FIGURE 6-7 EFFLUENT pH AS A FUNCTION OF SLUG SIZE

then decreasing to the pH of the brine. The 280 cc (0.373 pore volume) slug seems to be a combination of the two other profiles. For slugs of 105 cc (0.14 pore volume), 250 cc (0.33 pore volume), 280 cc (0.373 pore volume), and 325 cc (0.433 pore volume), increasing the slug size tends to increase the magnitude of the effluent pH. Increasing the slug size from 325 cc (0.433 pore volume) to 402 cc (0.536 pore volume) only resulted in an increase in the amount of full strength, unspent sodium hydroxide in the effluent.

Run 4006 was conducted with a 1.0 percent sodium hydroxide 105 cc (0.14 pore volume) slug to observe the effect on oil recovery of changing slug concentration. The use of 1.0 percent sodium hydroxide resulted in significantly higher recoveries as illustrated in Figures 6-8 and D-2. The recovery at water breakthrough of 17.5 percent was similar to the 0.1 percent slug recovery at breakthrough of 15.55 percent, recovery at 0.5 pore volume injected was 36.0 percent compared to 29.16 percent for the 0.1 percent sodium hydroxide slug. By 0.8 pore volume injected the 105 cc (0.14 pore volume) slug of 1.0 percent sodium hydroxide had a higher cumulative recovery than all the slug sizes less than 325 cc.

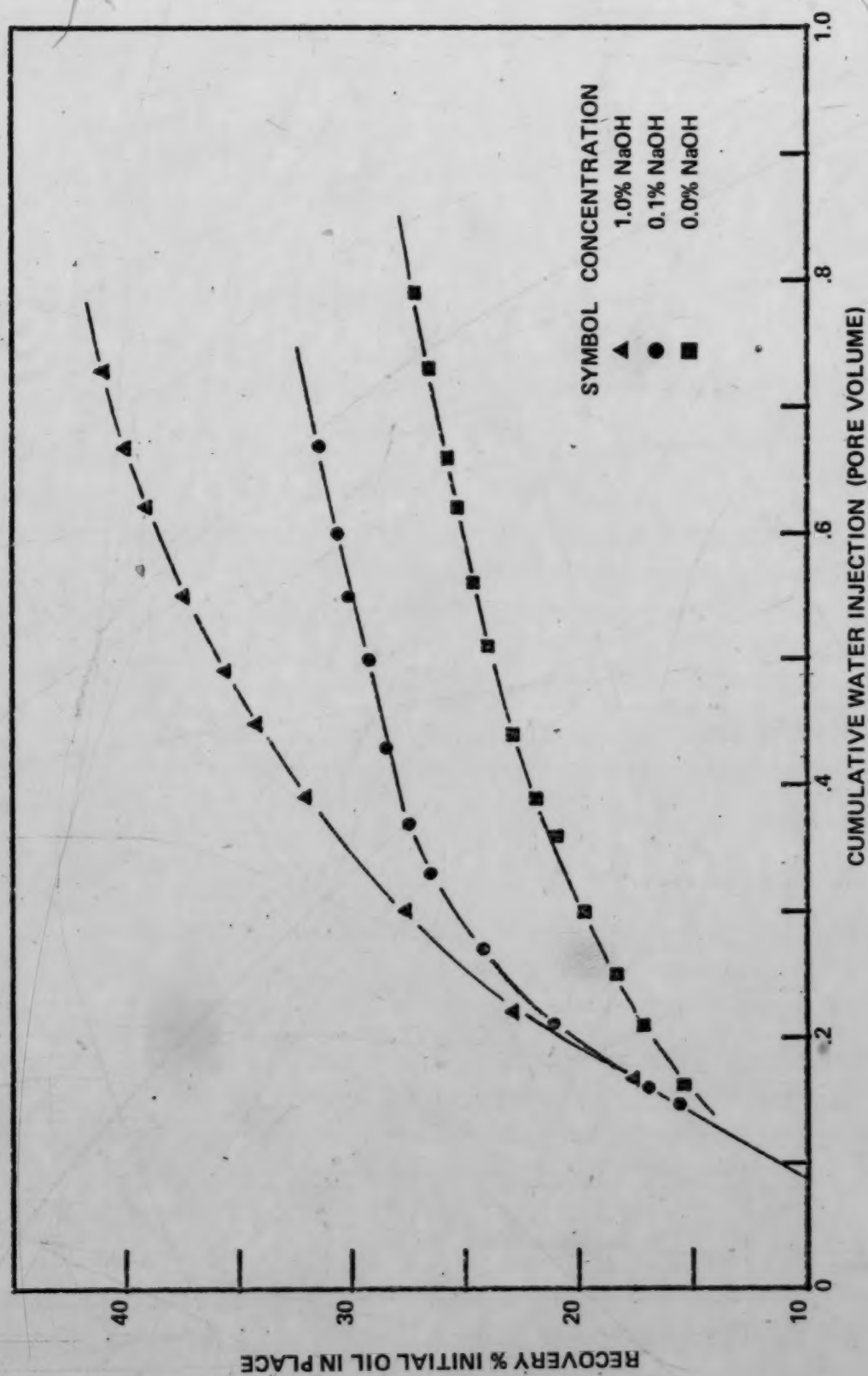


FIGURE 6-8 COMPARISON OF RECOVERY FOR DIFFERENT CONCENTRATIONS IN 105 cc SLUGS

The pH profile of the effluent during the 105 cc (0.14 pore volume) slug runs is presented in Figure 6-9. Both the 1.0 percent sodium hydroxide slug and the 0.1 percent sodium hydroxide slug have similar profiles except for the curve shift due to differences in slug concentration. The pH decline of the 1.0 percent curve was less rapid right after breakthrough but continues longer than the 0.1 percent curve. The effect of different concentrations of sodium hydroxide in the slug is illustrated in Figure 6-10. Although the number of data points is limited, it appears that recovery at breakthrough is not sensitive to slug concentration above 0.1 percent sodium hydroxide. Recoveries at water-oil ratios of 3.0 and 7.0 increase gradually as slug concentration is increased.

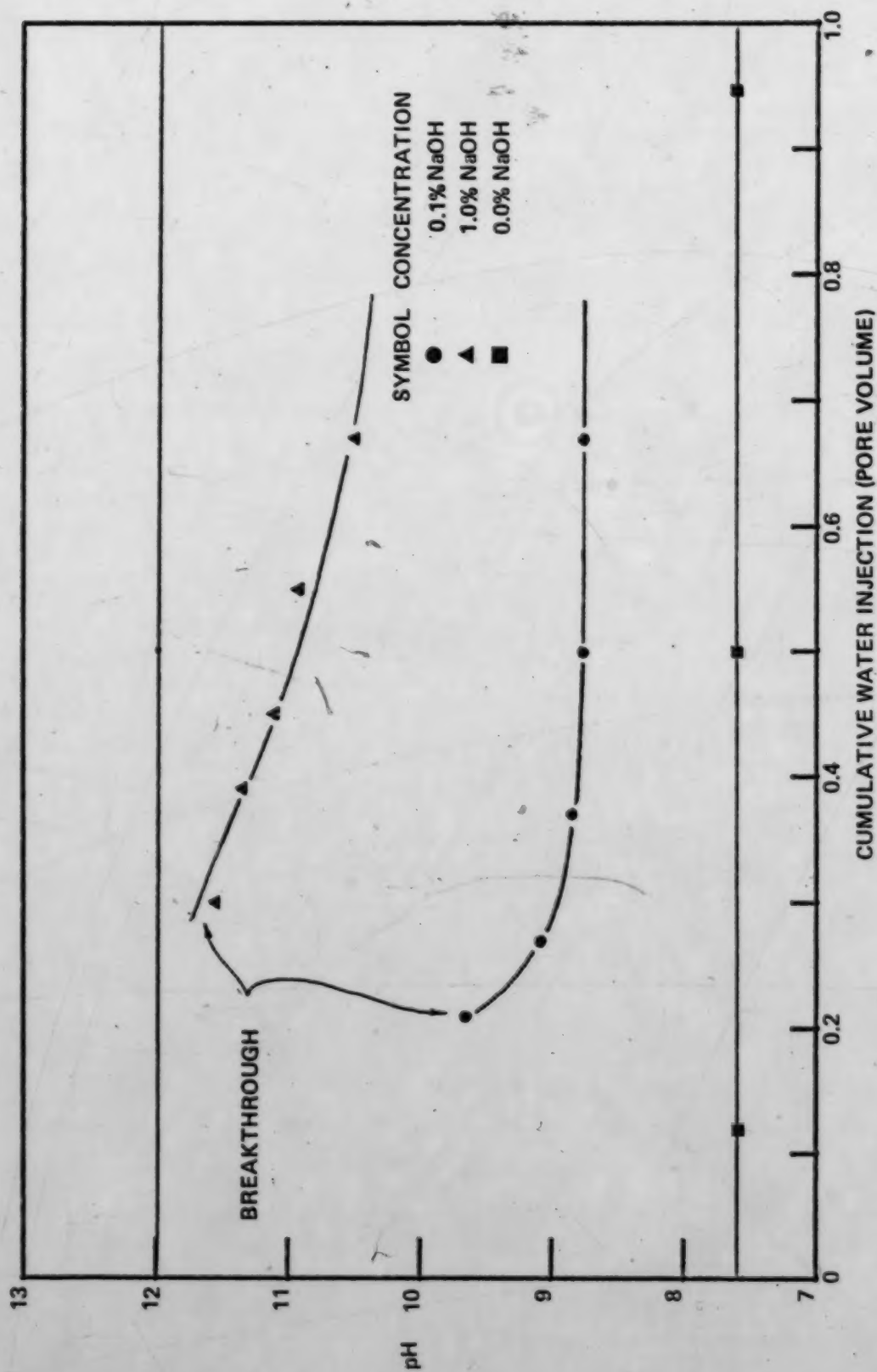


FIGURE 6-9 COMPARISON OF pH PROFILES OF 105 cc SLUGS WITH DIFFERENT SODIUM HYDROXIDE CONCENTRATION

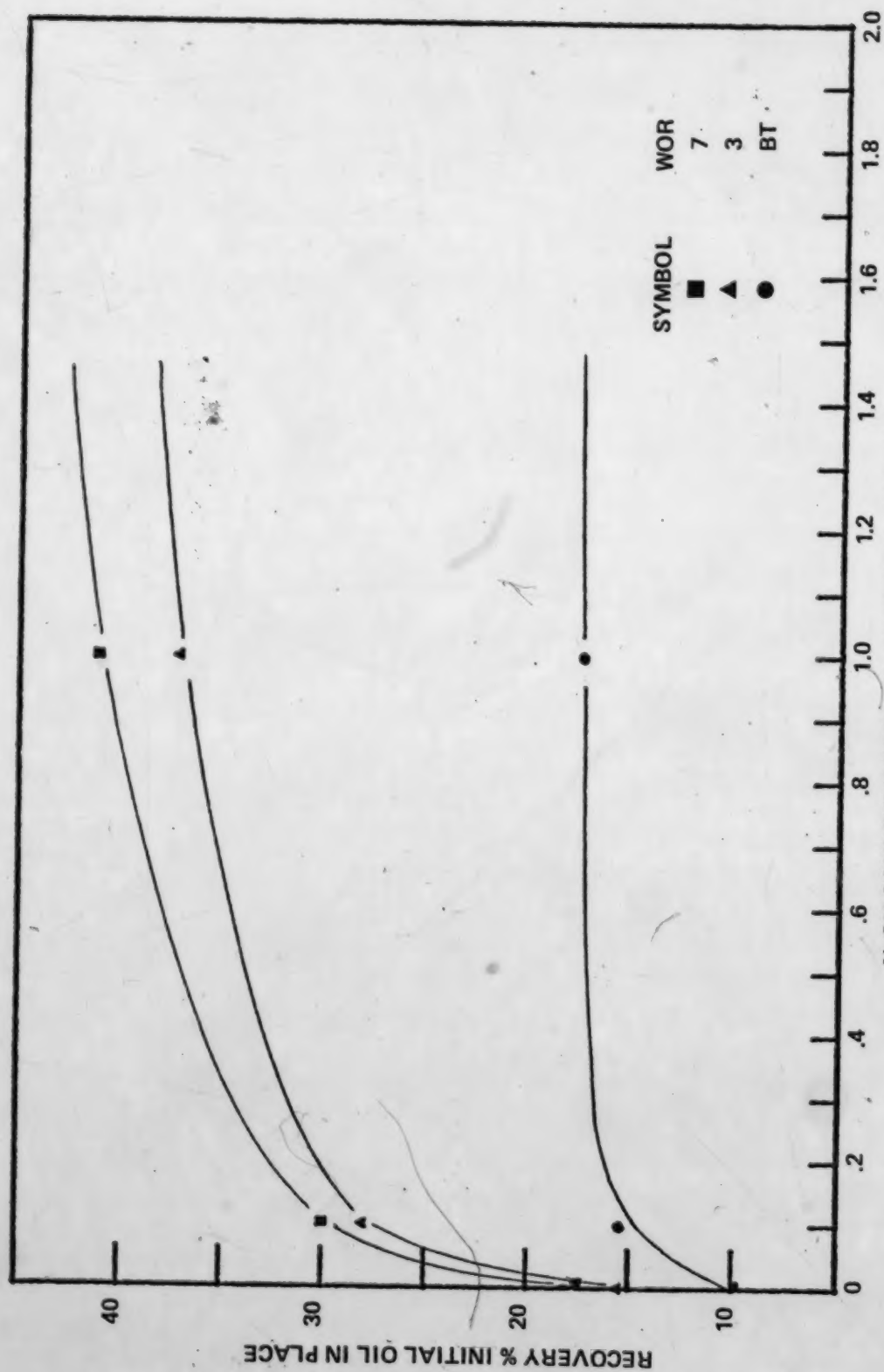


FIGURE 6-10 THE EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON THE RECOVERY OF A 105 cc SLUG

DISCUSSION

In previous studies employing sodium hydroxide as an additive to increase water flood recovery several reasons have been given for increased recovery. Some authors^{36,3} have stated that increased recovery is due to a change of wetting caused by chemical reaction at the sand surface. This would result in the removal from the sand surface of oil that previously would not be recovered. Other authors^{4,45,46} have suggested increased recovery was due to the reduction of the oil-water interfacial tension, making it easier to push the oil droplets through the constrictions in the pores of the porous medium.

Scott⁴¹, in his study, suggested that an oil-water emulsion was formed in the core by the sodium hydroxide solution, plugging the path of least resistance. This would force the displacing fluid into more resistant paths that would in turn be plugged by the emulsion until all paths are plugged. The emulsion would then be pushed through the core, displacing oil ahead of it (improved mobility ratio).

Reisberg et al.³⁹ found that sodium hydroxide reacted with the components of Ventura crude to change the wetting characteristics of the sand.

Both a change in wetting and a reduction of interfacial tension were observed in this study. The Sparky sand used was initially oil-wet according to the results of the imbibition and bench tests. Wettability tests conducted on the sand after it had been contacted by the sodium hydroxide indicated that it had been made less oil-wet. The shift in the relative permeability (Figure E-2) obtained when sodium hydroxide was used in the displacing phase seemed to confirm a wetting change.

Very low concentrations of sodium hydroxide in brine reduced Lloydminster crude - sodium hydroxide in brine solution interfacial tension to very low values, as illustrated in Table A-5. Concentrations greater than 0.005 percent sodium hydroxide in brine resulted in interfacial tension values less than the minimum measureable value with the du Nouy tensiometer of 0.5 dyne/cm.

It is possible that increased recoveries are due to both a wetting change and a reduction of the interfacial tensions. It should be noted that wettability and interfacial tension are interrelated and an adjustment to one would affect the other.

Whatever the displacement mechanism may be, it is evident that there is a minimum sodium hydroxide concentration required in order to increase recovery.

If the concentration is less than the minimum required, the displacement mechanism is not significantly activated and only minimal increases in recovery are realized. If only a portion of the core is contacted by sodium hydroxide solution with the minimum required concentration then increased recoveries are obtained from only that portion of the core.

Tests conducted using sodium hydroxide added to the entire injected fluid indicated that an approximate minimum injection concentration of 0.1 percent by weight sodium hydroxide is required for the system used in the study. An exact value of the minimum required concentration is impossible to obtain due to concentration changes after the solution has entered the core. The sodium hydroxide injection concentration must be high enough to compensate for dilution, reaction losses and absorption to allow the whole core to be contacted by sodium hydroxide solution with a concentration greater than the minimum required.

If sodium hydroxide is added to the entire injected fluid, as in the 3000 series of runs, maximum recoveries will result as long as the injection concentration is higher than the minimum required concentration. All the reservoir will be contacted by the injected fluid with the minimum required concentration.

Although the produced effluent at breakthrough had a reduced pH due to dilution, adsorption, and possibly chemical reaction, the effluent pH increased to injection strength when more of the displaced phase was produced. Since this indicates that injected fluid is passing through the core without loss of sodium hydroxide to reaction, dilution and adsorption, it can be assumed that no significant amount of unflooded core is being contacted.

The addition of sodium hydroxide to all of the injected fluid is unnecessary. A slug of sodium hydroxide solution displaced through the core by brine, if properly designed, would obtain the same increased recovery.

The slug must contain enough sodium hydroxide to provide for all losses in the core from injection to production, while maintaining a sodium hydroxide concentration higher than the minimum required concentration. There are two possible methods of achieving this. The first is to inject a large low-concentration slug; the second is to inject a small high-concentration slug (small, high concentration slugs tend to be more sensitive to fingering and bypassing). In the study, it was assumed that the recovery achieved when using an infinite slug (sodium hydroxide added to all the injected fluid)

of 0.1 percent sodium hydroxide brine solution was the maximum recovery possible with sodium hydroxide solutions. This recovery was used as a comparison for subsequent tests using different slug sizes.

Slugs of 325 cc (0.433 pore volume) and 402 cc (0.536 pore volume) of 0.1 percent sodium hydroxide, pushed through the core by brine, produced recoveries equal to that of the infinite slug. The 280 cc (0.373 pore volume) and smaller slugs produced only a portion of infinite slug recovery. It can be concluded that for this system the optimum 0.1 percent sodium hydroxide slug size is approximately 300 cc (0.40 pore volume) as indicated by Figure 6-6.

Inspection of the effluent pH profile (Figure 6-7) of the different slug sizes indicates that the best recoveries were obtained when the effluent pH approached the injection pH of 11.98, at or after breakthrough. For the 325 cc (0.433 pore volume), 402 cc (0.536 pore volume) and infinite slug sizes, effluent pH values of 11.8 or greater were measured. The smaller, less successful, slug sizes had effluent pH values much smaller than the injected pH. This would indicate that smaller slug sizes were being used up, or dissipated, prior to breakthrough. The dissipation of the slug could be due to the expected dilution, adsorption and chemical

reaction using up the sodium hydroxide at the leading edge of the slug. It could also be caused by fingering of the pushing brine at the trailing edge of the slug.

The pH profile of the 325 cc (0.433 pore volume) and 402 cc (0.536 pore volume) slugs exhibit low pH values at breakthrough which would indicate that the chemical in the leading edge of the slug is being used up.

The slow drop in pH at the trailing edge of the slug might be interpreted as being due to mixing of the slug and the pushing brine which is a miscible type of displacement (i.e. water displacing water). The fluctuation of water-oil ratio (Figure D-1) could also be attributed to mixing at the trailing edge of the slug.

It is possible that if mixing by the pushing brine was negated, much smaller, more economical slugs could achieve maximum recoveries. Mixing at the trailing edge of the slug could be drastically reduced by separating the sodium hydroxide slug and the pushing brine with a mobility buffer of polymers similar to that used in micellar-slug flooding.

Results of the use of a 105 cc (0.14 pore volume) slug of 1.0 percent sodium hydroxide suggested that increasing the slug concentration greatly improved the recovery of small slugs. The pH profile (Figure D-7)

indicates that this increased sodium hydroxide concentration makes it possible for the slug to withstand more mixing than the 0.1 percent sodium hydroxide before dropping below the minimum required concentration. The higher concentration would initially result in sharp concentration change in the core which, according to Moore et al.³⁴ would achieve higher recoveries.

A calculation was made for an idealized system (Appendix F) based on the results of the study to estimate the increased recovery and the amount of sodium hydroxide required for an oilfield scale enhanced recovery project. Linear displacement and 100 percent volumetric sweep were assumed. It was found that, by injecting a 0.4 pore volume slug of 0.1 percent sodium hydroxide in water, 384,300 barrels could be recovered from 40 acres of 10 foot thick Lloydminster-Sparky reservoir at a water-oil-ratio of 10. This would require 135,235 pounds of sodium hydroxide in a 450,000 barrel slug.

CONCLUSIONS

The following conclusions are based on the results of this experimental investigation of the effects of sodium hydroxide slug size and concentration on the recovery of viscous crude oil.

1. Recoveries of 40-45 percent of the initial oil-in-place can be achieved at a water-oil ratio of 10 when sodium hydroxide in sufficient concentrations is injected into a clean, sorted, Sparky sand core saturated with Lloydminster crude. A previous investigation by Scott⁴¹ obtained similar results.
2. Concentrations of 0.005 percent sodium hydroxide in brine will lower Lloydminster crude oil interfacial tension to less than 0.5 dyne/cm. These results are similar to those obtained by Cooper¹¹ and Scott⁴¹ in previous investigations.
3. To obtain significant increases in recovery from a Lloydminster-Sparky sand type system when flooding with sodium hydroxide in brine, concentrations of 0.1 percent by weight sodium hydroxide are required confirming results previously presented by Scott⁴¹.

4. A 0.4 pore volume slug of 0.1 percent by weight sodium hydroxide in brine followed through the core by brine achieves a recovery equivalent to that of an infinite slug of 0.1 percent sodium hydroxide.
5. Extensive dilution occurs at the trailing edge of the sodium hydroxide slug due to mixing.
6. Increasing the sodium hydroxide concentrations of the smaller slug sizes will result in increased recoveries.
7. Tests conducted on the Sparky sand used in this study indicate that it was preferentially oil-wet confirming similar results presented by Scott⁴⁰ and Scott⁴¹.
8. Sodium hydroxide, in contact with an oil-wet sand system, will cause the sand to become less oil-wet, or neutral.

RECOMMENDATIONS

From the data presented in this thesis the following recommendations can be made:

1. A further reduction of the required slug size can be achieved if fingering at the trailing edge of the sodium hydroxide slug was inhibited. Use of a polymer mobility buffer to separate the sodium hydroxide and the brine should be investigated.
2. Further study should be directed at the possibility of increasing recovery by the use of small, high concentration slugs of sodium hydroxide.
3. As viscous fingering is a function of the velocity at which one fluid displaces another, it is possible that lower injection rates would reduce the amount of mixing at the trailing edge of the slug. The effects of various injection rates on mixing of the brine into the sodium hydroxide slugs should also be investigated. It should be noted that actual reservoir velocities are low and decrease with distance from the injection well.

4. More knowledge of the actual microscopic effects of injecting sodium hydroxide into a porous medium saturated with viscous crude oil would be invaluable. To properly design a sodium hydroxide recovery process the displacement mechanism and its effects on the fluid properties must be known.
5. In order for sodium hydroxide to be used as a reservoir recovery process, further investigation of the interaction between the sodium hydroxide and natural field water should be conducted. Previous investigators have indicated that mixing of sodium hydroxide with field water has resulted in formation of a precipitate.
6. The use of sodium hydroxide causes the production to be in the form of an emulsion and further studies should be conducted on emulsions and methods of breaking emulsions. In this study, sodium hydroxide injection was treated as a primary recovery process.
7. Further tests should be conducted on flooded-out cores to observe if sodium hydroxide injection is applicable as a secondary recovery process.

BIBLIOGRAPHY

1. Adam, N.K., The Physics and Chemistry of Surfaces, Oxford University Press, London, (1941).
2. A.S.T.M., Standards of Petroleum Products, 1956
3. Bartell, F.E., and Miller, F.E., "Displacement of Crude Oil in Benzene From Silica by Aqueous Solutions", Industrial Engineering Chemistry, 335, Vol. 24, No. 3, (1932).
4. Beckstrom, R.C., and Van Tuyl, F.M., "The Effect of Flooding Oil Sands With Alkaline Solutions", Bulletin of the American Association of Petroleum Geologists, 11, 223, (1927).
5. Benner, F.C., and Bartell, F.E., "The Effect of Polar Impurities upon Capillary and Surface Phenomena in Petroleum Production", A.P.I. Drilling and Production Practice, 341, (1941).
6. Bobek, J.E., Mattax, C.C., and Denekas, M.O., "Reservoir Rock Wettability - Its Significance and Evaluation", Transactions A.I.M.E., Vol. 213, 155, (1958).
7. Calhoun, J.C., Stahl, C.D., Preston, F.W., and Nielson, R.F., "A Review of Laboratory Experiments on Wetting Agents for Water Flooding", Producers Monthly, 16 (1), 15-23, (1951).
8. Chuoke, R.L., van Meurs, P., and van der Poel, C., "The Instability of Slow Immiscible, Viscous Liquid-Liquid Displacement in Permeable Media", Transactions A.I.M.E., 216, 188-194, (1959).
9. Collins, H.N., "High Viscosity Crude Oil Displacement in a Long Unconsolidated Sand Pack Using a Native Brine", M.Sc. Thesis, University of Alberta, Department of Chemical and Petroleum Engineering. (1964).
10. Collins, R.E., Flow of Fluids Through Porous Materials, Reinhold Publishing Co., New York, (1961).

11. Cooper, R.J., "The Effect of Temperature on Caustic Displacement of Crude Oil", A.I.M.E. Reprint, Paper No. S.P.E. 3685, (1974).
12. Davis, J.T., and Ridel, E.K., "Interfacial Phenomena", Academic Press, New York, (1961).
13. de Haan, H.J., "The Effects of Capillary Forces in the Water Drive Process", Fifth World Petroleum Congress, Section II, 25 and Section II, 319, (1959).
14. DeVault, D., "The Theory of Chromatography", Journal of American Chemistry Soc., 65, 532-540, (1943).
15. Dodd, C.G., Moore, J.W., and Denekas, M.O., "Metaliferous Substances Adsorbed at the Crude Petroleum - Water Interfaces", Industrial and Engineering Chemistry, 44, 2585, (1952).
16. Donaldson, E.C., Thomas, R.D., and Lorenz, P.B., "Wettability Determination and Its Effects on Recovery Efficiency", S.P.E. Journal, (March, 1969).
17. Dunning, H.N., "The Interfacial Activity of Mesoporphyrin IX and Some Derivatives", Journal of Colloid Sci., 8, 279, (1953).
18. Dunning, H.N., and Johanson, R.T., "Laboratory Evaluation of Water Additives for Petroleum Displacement", R.I. 5352, U.S.B.M., (July, 1957).
19. Ehrlich, R., Hasiba, H.H., and Raimond, P., "Alkaline Water Flooding for Wettability Alteration - Evaluating a Potential Field Application", Journal of Petroleum Technology, (December, 1974).
20. Fazil, M., "High Viscosity Crude Oil Displacement in a Long Unconsolidated Natural Sand Pack Using Carbonated Brine", M.Sc. Thesis, Department of Chemical and Petroleum Engineering, University of Alberta, (1965).
21. Froning, H.R., and Leach, R.O., "Determination of Chemical Requirements and Applicability of Wettability Alteration Flooding", Journal of Petroleum Technology, (June, 1967).

22. Garrett, H.E., Surface Active Chemicals, Pergamon Press, Toronto, (1972).
23. Geffen, T.M., Owens, W.W., Parrish, D.R., and Morse, R.A., "Experimental Investigation of Factors Affecting Laboratory Relative Permeability Measurements", Trans. A.I.M.E., 192, 99, (1956).
24. Gibbs, J.W., Collected Work, Longhorns, Green, and Co., New York, 219, (1928).
25. Guerrero, E.T., "Practical Reservoir Engineering", The Petroleum Publishing Co., Tulsa, (1968).
26. Grave, D.J., and Johnson, C.E., Jr., "Field Trail of Caustic Water Flood Process", Journal of Petroleum Technology, (December, 1974).
27. Jennings, H.Y., Jr., Johnson, C.E., Jr., and McAuliffe, C.D., "A Caustic Water Flood Process for Heavy Oils", Journal of Petroleum Technology, (December, 1974).
28. Jennings, H.Y., Jr., "Surface Properties of Natural and Synthetic Porous Media", Producers Monthly, 21, No. 5, 20, (1957).
29. Jennings, H.Y., Jr., "Effect of Laboratory Core Cleaning on Water-Oil Relative Permeability", Producers Monthly (August, 1958).
30. Johnson, C.E., Jr., "Evaluation of Surfactants for Oil Field Flooding", Journal of American Oil Chemists Society, 34, 209, (1957).
31. Leach, R.O., and Wagner, O.R., "Improving Oil Displacement Efficiency by Wettability Adjustment", Trans. A.I.M.E., 216, 65, (1959).
32. Leach, R.O., Wagner, O.R., Wood, H.W., and Harpke, C.F., "A Laboratory and Field Study of Wettability Adjustment in Waterflooding", Journal of Petroleum Technology p. 205, (February, 1962).
33. Maguss, H., "A Laboratory Model Study of Water Flood Behavior in Linear Systems", M.Sc. Thesis, University of Alberta, (1962).

34. Moore, T.F., and Blum, H.A., "Importance of Wettability in Surface Active Agent Water Flooding", Oil and Gas Journal (December, 1958).
35. Mungan, N., "Interfacial Effects in Immiscible Liquid-Liquid Displacement in Porous Media", S.P.E. Journal, p. 247, (September, 1966).
36. Nutting, P.G., "Chemical Problems in the Water Driving of Petroleum From Oil Sands", Ind. and Eng. Chem., 17, p. 1035-1036, (1923).
37. Preston, F.W., and Calhoun, J.C., "Applications of Chromatography to Petroleum Production Research", Producers Monthly, 16, No. 5, 22, (March, 1952).
38. Rapoport, L.A., and Leas, W.J., "Properties of Linear Water Floods", Trans. A.I.M.E., 198, 139, (1953).
39. Reisberg, J., and Doscher, T.M., "Interfacial Phenomena in Crude Oil - Water Systems", Producers Monthly, 21, No. 1, p. 43, (November, 1956).
40. Scott, G.R., "Improving Water Flood Recovery of Viscous Crude Oils by Chemical Control", M.Sc. Thesis, Department of Chemical and Petroleum Engineering, University of Alberta, (1965).
41. Scott, J.D., "Controlled Chemical Water Flooding of Viscous Crude Oil", M.Sc. Thesis, Department of Chemical and Petroleum Engineering, University of Alberta, (1971).
42. Snell, F.D., and Snell, C.T., "Surface Activity as Applied to Secondary Petroleum Production", World Oil, (November, 1951).
43. Taber, J.J., "The Injection of Detergent Slugs in Water Floods", Trans. A.I.M.E., 213, 186, (1958).
44. Taber, J.J., "Dynamic and Static Forces Required to Remove a Discontinuous Oil Phase From Porous Media Containing Both Oil and Water", S.P.E.J., (March, 1969).

45. Terwilliger, P.L., and Yuster, S.T., "Chemical Agents in Water Flooding", Tenth Petroleum Production Conference, 41, (1947).
46. Uren, L.C., and Fahmy, E.H., "Factors Influencing the Recovery of Petroleum from Unconsolidated Sands by Water Flooding", Trans. A.I.M.E., 318, (1927).
47. Warren, J.E., and Calhoun, J.C., "A Study of Water Flood Efficiency in Oil-Wet Systems", Trans. A.I.M.E., 204, 22, (1955).
48. Weiser, J.B., Colloid Chemistry, John Wiley and Sons, New York, (1950).
49. Westfall, M.F., "Secondary Recovery Attempts on Lloydminster Asphaltic Crude Oil", Producers Monthly, (June, 1962).

APPENDIX A

PHYSICAL PROPERTIES OF THE ROCKS AND FLUIDS

TABLE A-1

Golpher Sand

<u>Mesh Size</u>	<u>Aperature Diameter (inches)</u>	<u>Weight Retained (gms)</u>	<u>Weight Flow Through (gms)</u>	<u>Cumulative Mass Fraction Through Screen</u>
14	1.41		869.5	1.0
20	0.841	8.5	861.0	0.9902
28	0.595	526.2	334.8	0.385
35	0.50	295.7	39.1	0.0454
48	0.297	34.6	4.5	0.0052
100	0.149	<u>4.5</u>		
		869.5		

TABLE A-2Sparky Sand

<u>Mesh Size</u>	<u>Aperature Diameter (inches)</u>	<u>Weight Retained (gms)</u>	<u>Weight Flow Through (gms)</u>	<u>Cumulative Mass Fraction Through Screen</u>
35	0.5		326.8	1.00
48	0.297		326.8	1.00
65	0.213	153.8	173.0	0.5294
100	0.149	110.3	62.7	0.1919
150	0.100	48.4	14.3	0.0439
200	0.074	<u>14.3</u>		
		326.8		

TABLE A-3

Viscosity of Lloydminster Crude

<u>Temperature, °F</u>	<u>Viscosity, Cp</u>
70.16	1780.95
90.00	932.82
122.00	239.86
147.20	96.46

Density of Lloydminster Crude

<u>Temperature, °F</u>	<u>Density, gm/cc</u>
70.16	0.9560
90.00	0.9495
122.00	0.9356
147.20	0.9115

TABLE A-4

Chemical Water Analysis

Lloydminster (Sparky Pool)

Conductivity-----87,000 ppm

Total Solids-----73,936 ppm

Hardness-----9,850 ppm

Chlorides-----44,400 ppm

Alkalinity-----40 ppm

Bicarbonate of Calcium and Magnesium

Iron-----18.25 ppm

Calcium-----2,640.0 ppm

Magnesium-----1,150.0 ppm

Sodium-----23,000 ppm

Potassium-----1,100 ppm

Copper-----0.08 ppm

Zinc-----0.10 ppm

Manganese-----0.4 ppm

Sulfates-----4.0 ppm

Alberta Department of Agriculture

TABLE A-5

Interfacial Tension

T = 76°F

<u>Concentration Sodium Hydroxide</u> <u>(percent by weight)</u>	<u>Interfacial Tension</u> <u>(dyne/cm)</u>
1.0	0.5
0.5	0.5
0.1	0.5
0.05	0.5
0.01	0.5
0.005	0.6
0.001	3.6
0.000 (Brine)	16.5

Surface Tension

T = 76°F

Brine	76.6 dyne/cm
Lloydminster Crude Oil	28.1 dyne/cm

TABLE A-6

Wettability MeasurementsBench Test

<u>Sand</u>	<u>Fluid</u>	<u>Rate of Movement Into Sand</u>
Fresh Sparky	Brine	Nil
	Varsol-Crude	Spontaneous
	Sodium Hydroxide-Brine	Nil
Sodium Hydroxide Contacted Sparky Sand	Brine	Slow
	Varsol-Crude	Rapid
	Sodium Hydroxide-Brine	Rapid

Imbibition Test 1

Saturating Fluid = 15 percent Lloydminster Crude in Varsol.

Sand = Fresh Sparky Sand.

Imbibing Fluid = Brine.

<u>Time, Min.</u>	<u>Total Imbibition, cc</u>
0	0.0
5	0.0
10	0.0
30	0.0
60	0.0
240	0.0
600	0.0

Imbibition Test 2

Saturating Fluid = 15 percent Lloydminster Crude in Varsol.

Sand = Fresh Sparky Sand.

Imbibing Fluid = 0.1 percent by Weight Sodium Hydroxide in Brine.

<u>Time Min.</u>	<u>Total Imbibition cc</u>
0	0.0
5	0.3
10	0.5
30	0.75
60	0.8
240	0.8
600	0.8

Imbibition Test 3

Saturating Fluid = 15 percent Lloydminster Crude in Varsol.

Sand = Sparky Sand Treated with Sodium Hydroxide

Imbibing Brine = Brine.



<u>Time Min.</u>	<u>Total Imbibition cc</u>
0	0.0
5	0.0
10	0.0
30	0.0
60	0.0
240	0.0
600	0.0

Imbibition Test 4

Saturating Fluid = 15 percent Lloydminster Crude in Varsol.

Sand = Sparky Sand Treated with Sodium Hydroxide

Imbibing Fluid = 0.1 percent by Weight Sodium Hydroxide in Brine.

<u>Time, Min.</u>	<u>Total Imbibition, cc</u>
0	0.0
5	0.4
10	0.65
30	1.05
60	1.05
240	1.1
600	1.1

TABLE A-7

pH as a Function of Sodium Hydroxide Concentration

<u>Sodium Hydroxide Concentration, weight percent</u>	<u>pH</u>
1.0	12.88
0.5	12.45
0.1	11.98
0.05	11.80
0.1	11.21
0.005	10.90

Temperature 76°F

TABLE A-8

Initial Core Properties

<u>TEST</u>	<u>RUN</u>	<u>SAND</u>	<u>CORE</u>	<u>TEMP.</u> ° F	<u>Swi</u> % P.V.	<u>K</u> Darcy	<u>φ</u> %
1	1001	1	1	102.0	7.0	37.73	32.45
2	1002	1	1	103.0	15.5	37.73	32.45
3	1003	1	1	103.0	15.9	37.73	32.45
4	1004	1	1	102.0	17.7	37.73	32.45
5	1005	1	1	106.0	29.4	37.73	32.45
6	2001	2	2	85.0	8.6	27.22	41.65
7	2002	2	3	86.9	6.4	24.50	39.18
8	2003	2	4	87.0	7.1	28.37	44.43
9	2004	2	4	87.0	20.9	28.37	44.43
10	3001	2	5	86.0	6.5	27.00	41.63
11	3002	2	6	85.0	7.1	27.68	38.19
12	3003	2	7	85.0	7.8	27.47	43.90
13	3004	2	8	88.0	4.6	21.82	38.40
14	4001	2	9	88.0	6.4	26.41	39.71
15	4002	2	10	87.0	6.7	24.50	43.31
16	4003	2	11	87.0	6.1	22.46	43.47
17	4004	2	12	87.0	4.9	24.50	43.09
18	4005	2	13	86.0	6.8	21.82	40.92
19	4006	2	14	86.0	5.3	22.65	42.88

* Sand Type 1 = Golpher Sand
Sand Type 2 = Sparky Sand

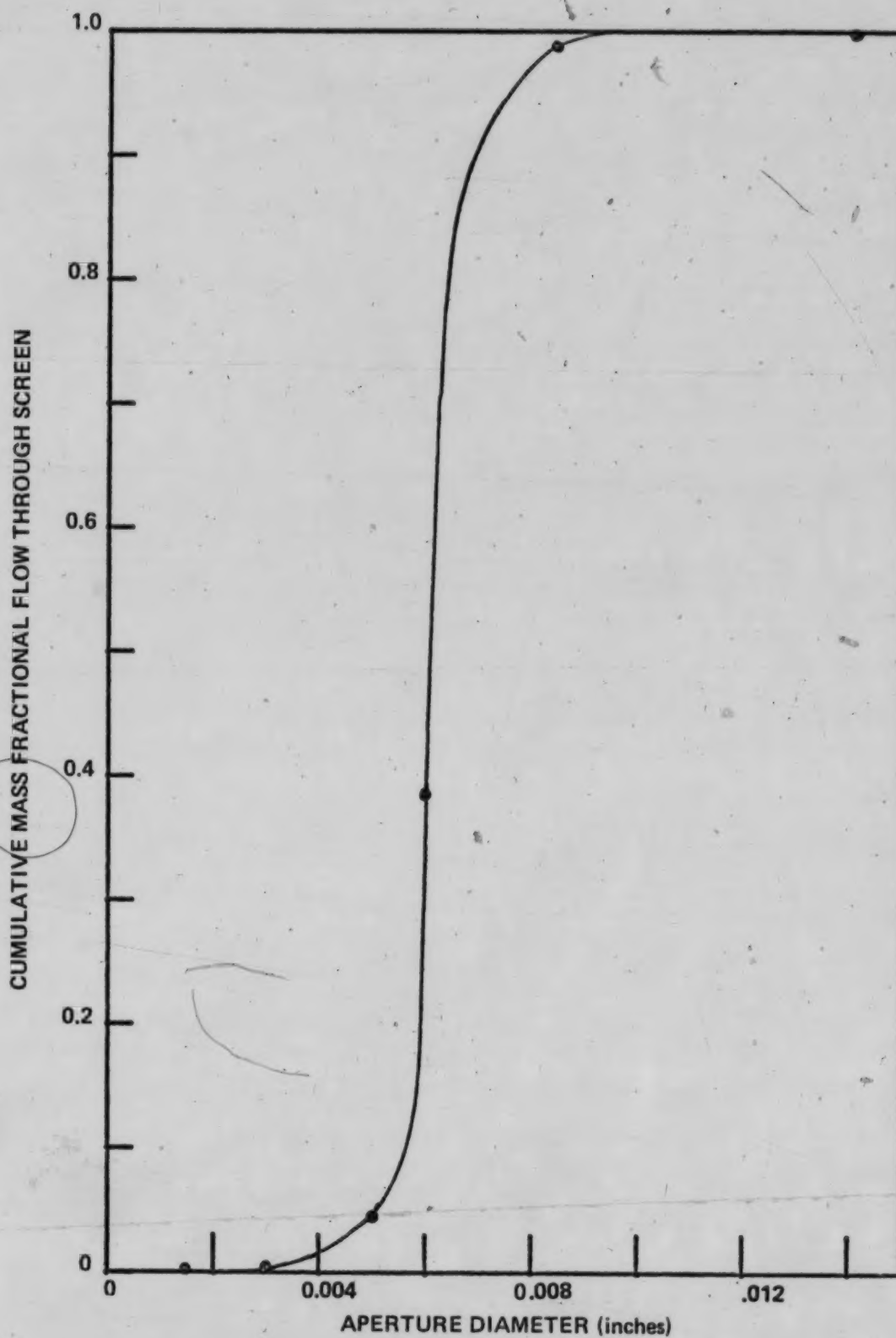


FIGURE A-1 PARTICLE SIZE DISTRIBUTION OF GOLPHER SANDS

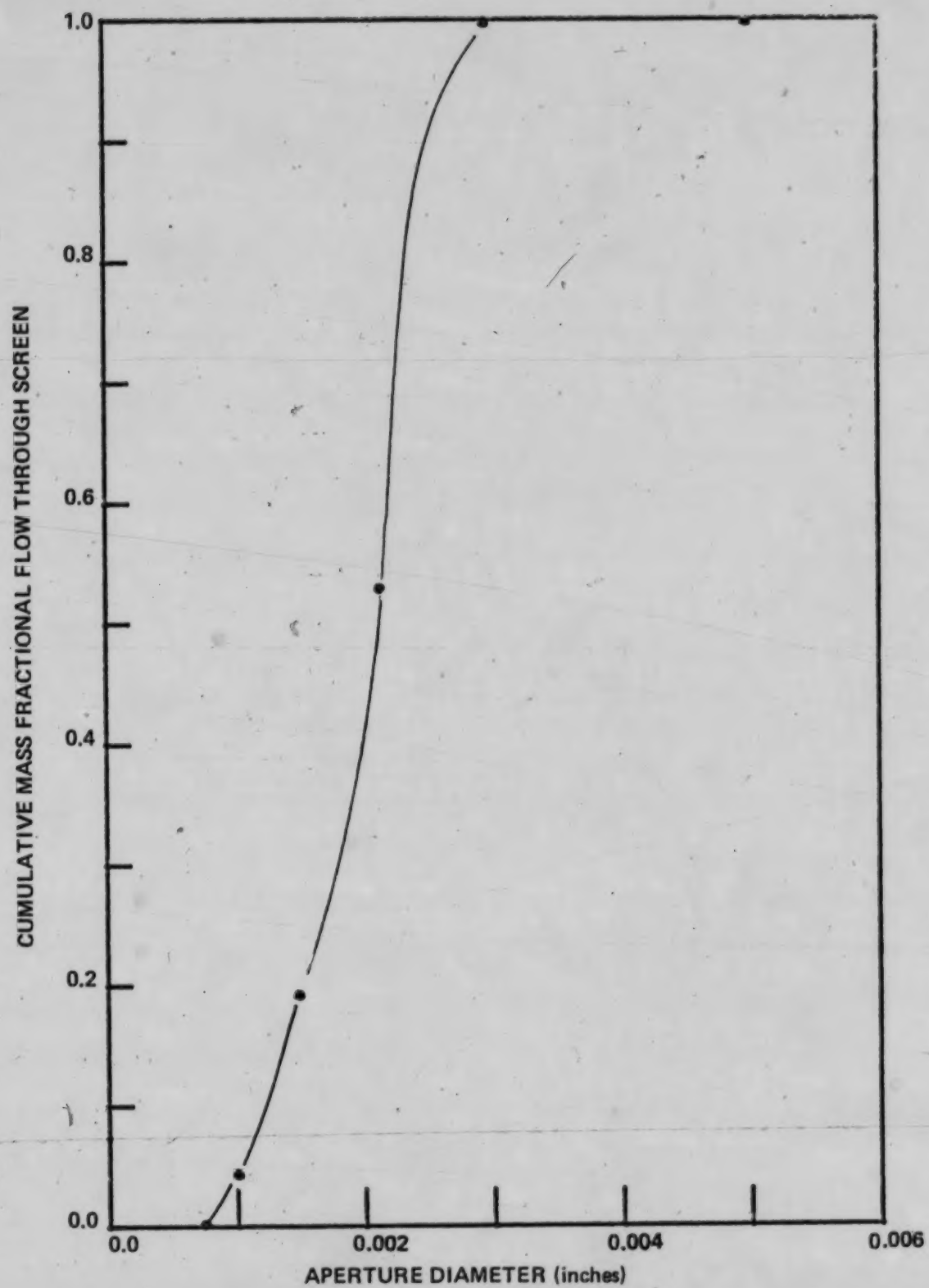


FIGURE A-2 PARTICLE SIZE DISTRIBUTION OF SPARKY SAND

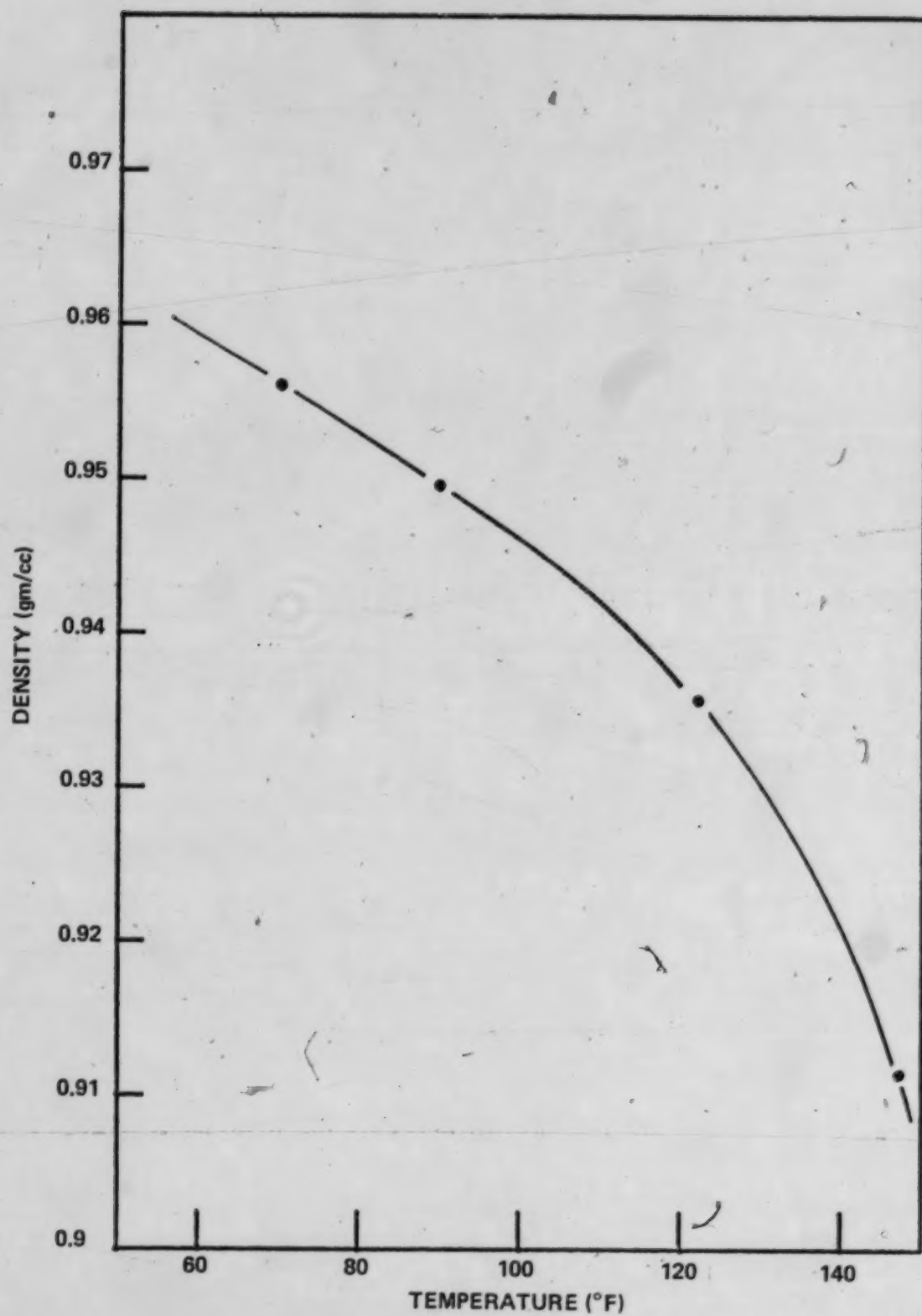


FIGURE A-3 DENSITY OF LLOYDMINSTER CRUDE AS
A FUNCTION OF TEMPERATURE

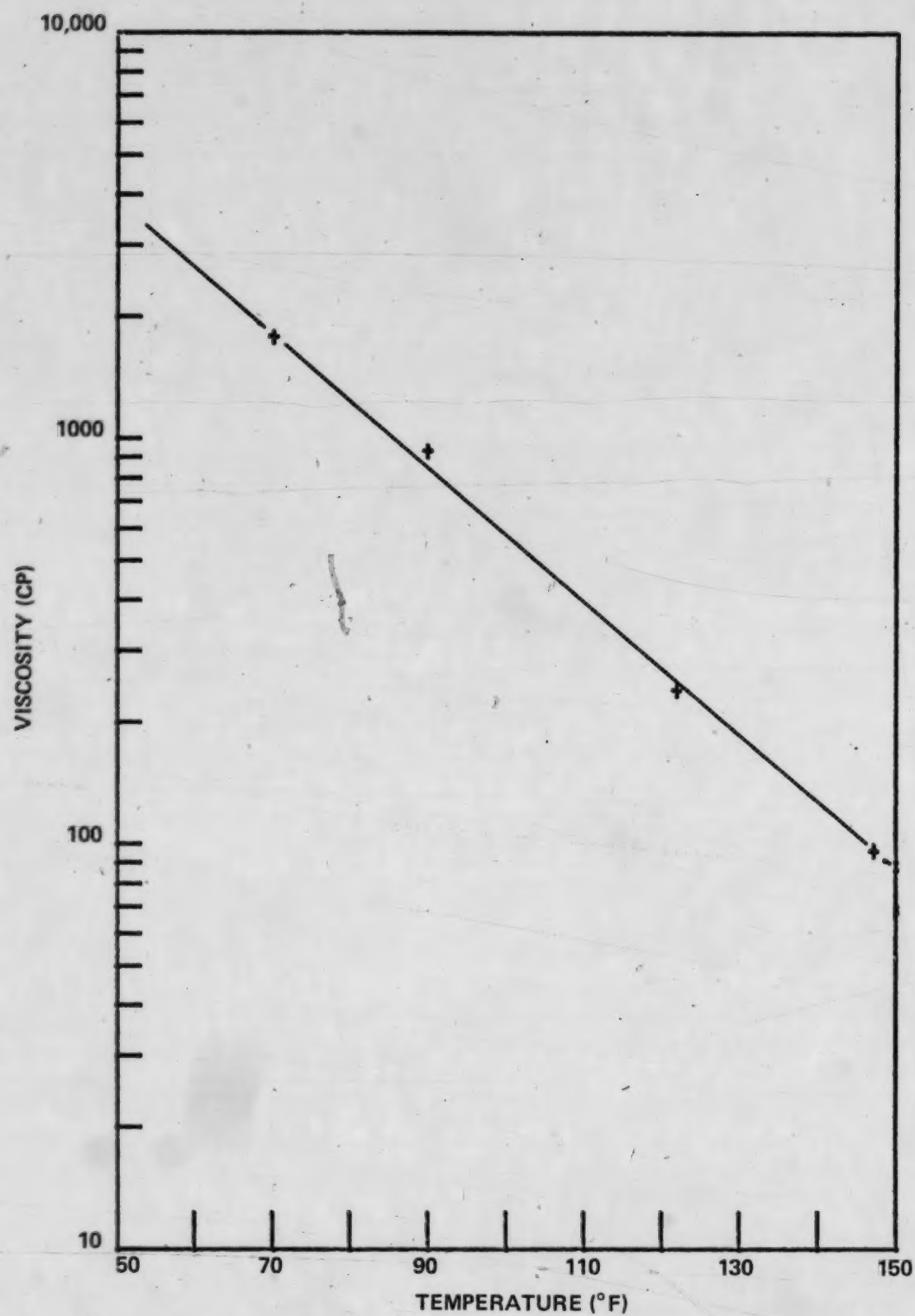


FIGURE A-4 VISCOSITY OF LLOYDMINSTER CRUDE AS A FUNCTION OF TEMPERATURE

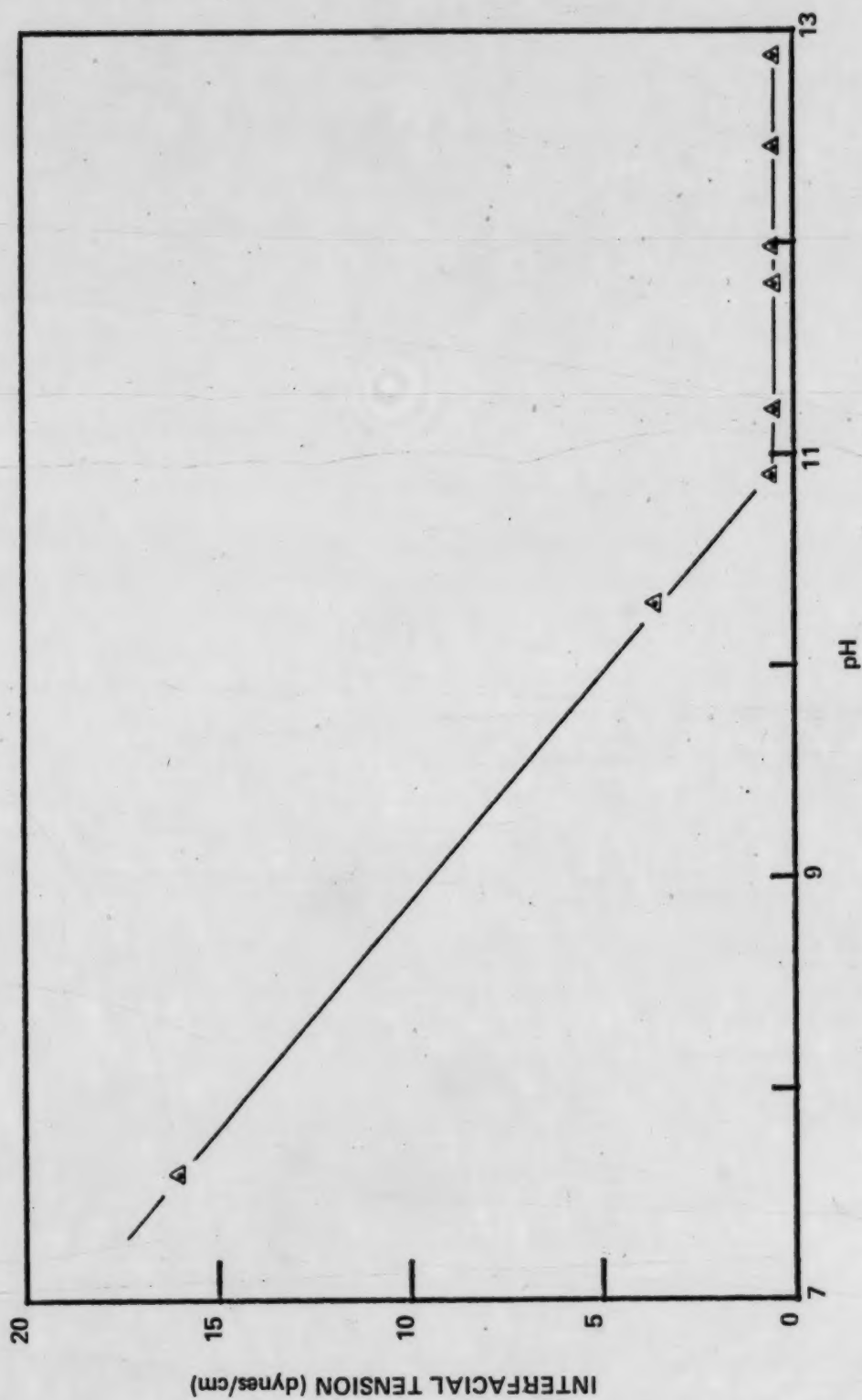


FIGURE A-5 INTERFACIAL TENSION AS A FUNCTION OF pH

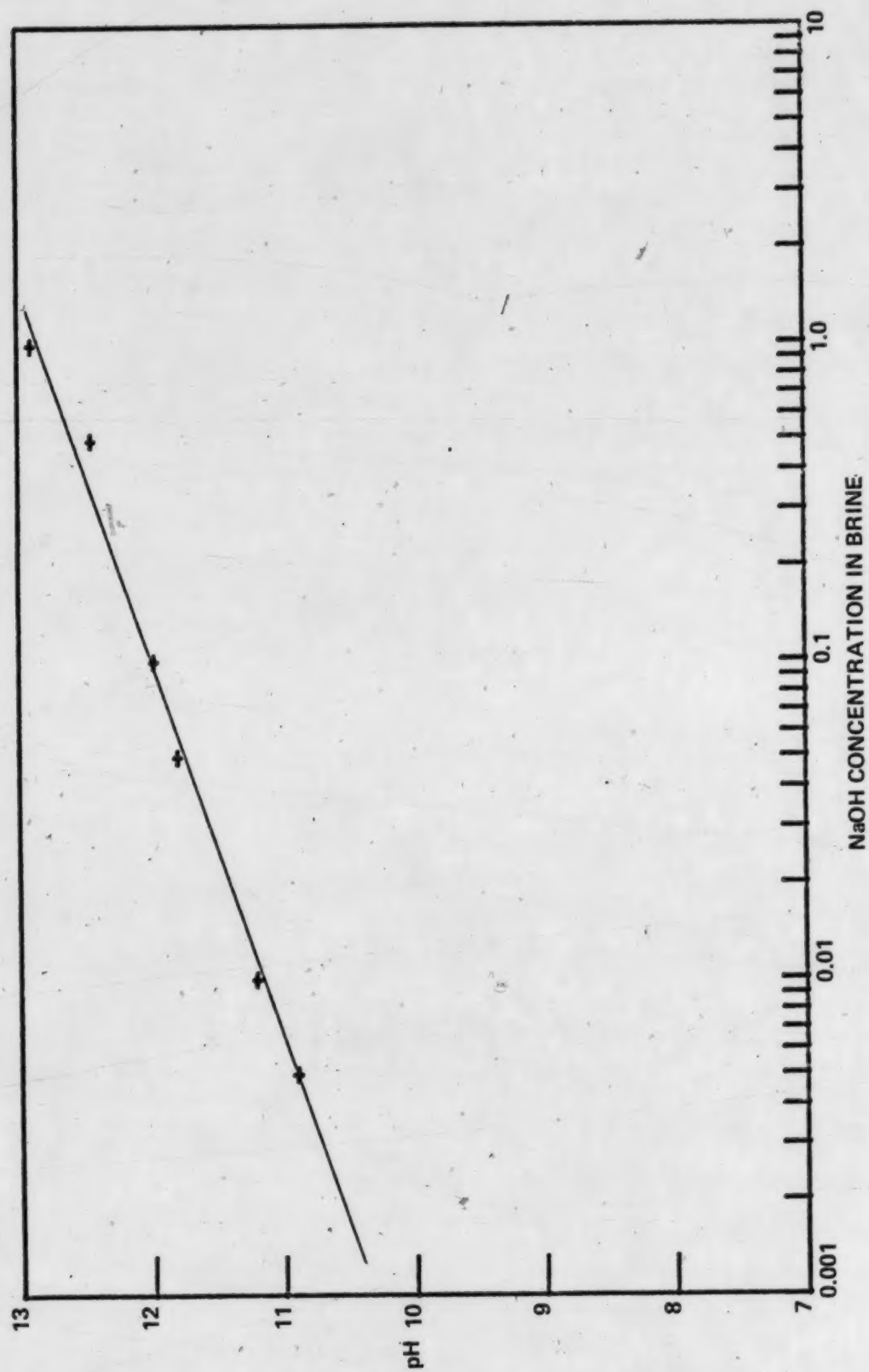


FIGURE A-6 pH AS A FUNCTION OF SODIUM HYDROXIDE CONCENTRATION IN BRINE

APPENDIX B

SUMMARY OF THE SCALING COEFFICIENTS

TABLE B-1

SUMMARY OF SCALING COEFFICIENTS

Rate cc/hr	Recovery % I.O.I.P.		Temperature °F	μ μ w	Yow	K $\times 10^{-8}$ cm ²	(1)	(2)	(3)
	B.T.	WOR=6	WOR=10				$\mu_w LV$	$\frac{LV \mu w}{Y \sqrt{K}}$	$\frac{C \sqrt{\frac{3\sigma}{V} \frac{w_0 K}{(\mu_0 - \mu w)}}}{\sqrt{V(\mu_0 - \mu w)}}$
60	16.7	44.5	47.5	778	25.4	37.43	3.82	0.04126	18.57
560	19.9	43.1	49.0	805	25.4	37.43	33.15	0.35761	6.20
120	14.9	44.0	48.8	778	25.4	37.43	7.65	0.08252	13.13
960	18.0	47.0	52.0	805	25.4	37.43	61.20	0.66020	4.56
520	19.5	48.5	51.0	679	25.4	37.43	33.15	0.35761	6.75

*

- (1) Rapoport and Leas Scaling Coefficient
 (2) de Haan Coefficient
 (3) Chuoke et al Coefficient.

APPENDIX C

SUMMARY OF DISPLACEMENT TEST CONDITIONS

TABLE C-1
SUMMARY OF DISPLACEMENT TESTS

Test	Run	Sand	Temperature °F	Rate cc/hr	SWI %	K darcys	Slug Size (cc)	NAOH % wt	Pore Volume (cc)
1	1001	1	102.0	560.0	7.07	37.73	*****	0.000	594
2	1002	1	103.0	60.0	15.53	37.73	*****	0.000	594
3	1003	1	103.0	120.0	15.92	37.73	*****	0.000	594
4	1004	1	102.0	960.0	17.73	37.73	*****	0.000	594
5	1005	1	106.0	520.0	29.41	37.73	*****	0.000	594
6	2001	2	85.0	320.0	8.61	27.22	*****	0.000	778
7	2002	2	86.9	320.0	6.42	24.50	*****	0.000	730
8	2003	2	87.0	320.0	7.10	28.37	*****	0.000	830
9	2004	2	87.0	480.0	20.90	28.37	*****	0.000	830
10	3001	2	86.0	320.0	6.56	27.00	*****	1.000	762
11	3002	2	85.0	320.0	7.15	27.68	*****	0.005	699
12	3003	2	85.0	320.0	7.80	27.47	*****	1.000	820
13	3004	2	88.0	320.0	4.69	21.82	*****	0.100	703
14	4001	2	88.0	320.0	6.46	26.46	250.0	0.100	727
15	4002	2	87.0	320.0	6.79	24.50	325.0	0.100	809
16	4003	2	87.0	320.0	6.15	22.46	280.0	0.100	812
17	4004	2	87.0	320.0	4.96	24.50	105.0	0.100	805
18	4005	2	86.0	320.0	6.80	21.82	402.0	0.100	749
19	4006	2	86.0	320.0	5.36	22.65	105.0	1.000	801

**** Sodium hydroxide added to the injected brine (infinite slug size)

* Sand 1 = Golpher
Sand 2 = Sparky

APPENDIX D

SUMMARY OF DATA FROM INDIVIDUAL
DISPLACEMENT TESTS

LIST OF SYMBOLS USED IN TABLE D

DWP	Water produced during time step
WP	Cumulative produced water
DNP	Oil produced during time step
NP	Cumulative oil produced
PIOP	Percent initial oil-in-place
WI(CC)	Cumulative water injected (cubic centimeters)
WI(PV)	Cumulative water injected (pore volumes)
DP(PSI)	Differential pressure across core (PSI)
PV	Pore volume
IOIP	Initial oil-in-place
SWI	Initial water saturation
***	Not measurable

TABLE D 1

RUN 1001
 TEMPERATURE = 102.000 DFGRFFS F
 RATE = 560.000 CC/HR
 SLUG SIZE = ***** CC
 CONCENTRATION = 0.000 PERCENT NAOH
 PV = 594.000 CC
 INIP = 552.000 CC
 PERMEABILITY = 37.731 DARCY
 SWI = 7.070 PERCENT
 POROSITY = 32.453 PERCENT
 OIL VISCOSITY = 595.000 CP

BREAK THROUGH = 110.00 CC 0.1851 PV 19.9275 PERCENT

DWP(CC)	WP(CC)	DNP(CC)	NP(CC)	PINP	WI(CC)	WI(PV)	WOR	DP(PSI)	PH
0.00	0.00	52.00	52.00	9.42	52.00	0.08	0.00	*****	*****
0.00	0.00	48.00	100.00	18.11	100.00	0.16	0.00	*****	*****
0.80	0.80	20.70	120.70	21.86	121.50	0.20	0.03	*****	*****
21.00	21.80	25.00	145.70	26.39	167.50	0.28	0.84	*****	*****
31.00	52.80	18.50	164.20	29.74	217.00	0.36	1.67	*****	*****
33.00	85.80	13.50	177.70	32.19	263.50	0.44	2.44	*****	*****
33.50	119.30	13.50	191.20	34.63	310.50	0.52	2.48	*****	*****
37.50	156.80	9.00	200.20	36.26	357.00	0.60	4.16	*****	*****
39.80	196.60	8.70	208.90	37.84	405.50	0.68	4.57	*****	*****
40.50	237.10	8.00	216.90	39.29	454.00	0.76	5.06	*****	*****
42.00	279.10	9.50	226.40	41.01	505.50	0.85	4.42	*****	*****
40.20	319.30	6.80	233.19	42.24	552.50	0.93	5.91	*****	*****
40.00	359.30	6.00	239.19	43.33	598.50	1.00	6.66	*****	*****
39.10	398.39	5.90	245.09	44.40	643.50	1.08	6.62	*****	*****
38.50	436.89	8.60	253.69	45.96	690.60	1.16	4.47	*****	*****
47.50	484.39	7.50	261.19	47.31	745.60	1.25	6.33	*****	*****
40.00	524.40	7.50	268.69	48.67	793.10	1.33	5.33	*****	*****
42.30	566.70	4.20	272.89	49.43	839.60	1.41	10.07	*****	*****
45.50	612.20	4.50	277.39	50.25	889.60	1.49	10.11	*****	*****

TABLE D 2

RUIN	1002	
TEMPERATURE	=	103.000
RATE	=	60.000
SLUG SIZE	=	*****
CONCENTRATION	=	0.000
PV	=	594.000
INIP	=	501.740
PERMEABILITY	=	37.734
SWI	=	15.531
POROSITY	=	32.450
OIL VISCOSITY	=	575.000
		CC
		CC
		DARCYS
		PERCENT
		PERCENT
		CP

BREAK THROUGH = 84.00 CC 0.1414 PV 16.7417 PERCENT

DWP(CC)	WP(CC)	DNP(CC)	NP(CC)	PIOP	WI(CC)	WI(PV)	WOR	NP(PST)	PH
0.00	0.00	52.00	52.00	10.36	52.00	0.08	0.00	*****	*****
0.00	0.00	22.00	74.00	14.74	74.00	0.12	0.00	*****	*****
6.20	6.20	25.80	99.80	19.89	106.00	0.17	0.24	*****	*****
16.50	22.70	20.50	120.30	23.97	143.00	0.24	0.80	*****	*****
16.00	38.70	14.50	134.80	26.86	173.50	0.29	1.10	*****	*****
25.50	64.20	16.50	151.30	30.15	215.50	0.36	1.54	*****	*****
30.20	94.40	9.60	160.90	32.06	255.30	0.42	3.14	*****	*****
27.30	121.70	11.49	172.39	34.36	294.10	0.49	2.37	*****	*****
30.20	151.90	9.80	182.19	36.31	334.10	0.56	3.08	*****	*****
25.80	177.69	11.40	193.59	38.58	371.30	0.62	2.26	*****	*****
36.80	214.49	9.00	202.59	40.37	417.10	0.70	4.08	*****	*****
33.00	247.49	7.00	209.59	41.77	457.10	0.76	4.71	*****	*****
39.00	286.50	7.50	217.09	43.26	503.60	0.84	5.20	*****	*****
48.00	334.50	7.50	224.59	44.76	559.10	0.94	6.40	*****	*****
34.20	368.69	4.59	229.19	45.68	597.89	1.00	7.43	*****	*****
38.50	407.19	4.50	233.69	46.57	640.89	1.07	8.55	*****	*****
23.80	430.99	2.70	236.39	47.11	667.39	1.12	8.81	*****	*****
35.00	465.99	3.00	239.39	47.71	705.39	1.18	11.66	*****	*****
25.00	490.99	2.00	241.39	48.11	732.39	1.23	12.50	*****	*****

TABLE D 3

RUN		1003	
TEMPERATURE =	=	103.000	DEGR FFS F
RATE =	=	120.000	CC/HK
SLOG SIZE =	=	*****#	CC
CONCENTRATION=	=	0.000	PERCENT NAOH
PV =	=	594.000	CC
IPIP =	=	499.400	CC
PERMEABILITY =	=	37.731	DARCS
SWI =	=	15.925	PERCENT
POROSITY =	=	32.453	PERCENT
OIL VISCOSITY=	=	575.000	CP

BRFAK THROUGH = 74.60 CC 0.1255 PV 14.9379 PERCENT

DWP(CC)	WP(CC)	DNP(CC)	NP(CC)	PINP	WI(CC)	WI(PV)	WNR	NP(PSI)	PH
0.00	0.00	4.50	4.50	0.90	4.50	0.00	0.00	0.00	0.00
0.00	0.00	37.00	41.50	8.30	41.50	0.06	0.00	0.00	0.00
0.00	0.00	26.60	68.10	13.63	68.10	0.11	0.00	0.00	0.00
1.10	1.10	14.90	83.00	16.61	84.10	0.14	0.07	0.00	0.00
2.50	3.60	7.50	90.50	18.12	94.10	0.15	0.33	0.00	0.00
3.50	7.10	8.50	99.00	19.82	106.10	0.17	0.41	0.00	0.00
19.80	26.90	23.00	121.99	24.42	148.90	0.25	0.86	0.00	0.00
25.50	52.40	19.50	141.50	28.33	193.90	0.32	1.30	0.00	0.00
32.00	84.40	16.80	158.30	31.69	242.69	0.40	1.90	0.00	0.00
40.00	124.40	15.00	173.30	34.70	297.70	0.50	2.66	0.00	0.00
35.50	159.90	11.00	184.30	36.90	344.20	0.57	3.22	0.00	0.00
47.80	207.70	12.20	196.49	39.34	404.20	0.68	3.91	0.00	0.00
13.50	221.20	3.50	199.99	40.04	421.20	0.70	3.85	0.00	0.00
37.50	258.70	8.00	207.99	41.64	466.70	0.78	4.68	0.00	0.00
41.50	307.20	7.50	215.49	43.15	515.70	0.86	5.53	0.00	0.00
36.00	336.20	6.00	221.49	44.35	557.70	0.93	6.00	0.00	0.00
39.00	375.20	5.50	226.99	45.45	602.20	1.01	7.09	0.00	0.00
39.80	415.00	5.20	232.19	46.49	647.20	1.08	7.65	0.00	0.00
44.80	459.80	6.20	238.39	47.73	698.20	1.17	7.22	0.00	0.00
36.00	495.80	4.00	242.39	48.53	738.20	1.24	9.00	0.00	0.00
22.00	517.80	2.00	244.39	48.93	762.20	1.28	11.00	0.00	0.00

TABLE D 5

RUN	1005		
TEMPERATURE	=	106.000	DEGREES F
RATE	=	520.000	CC/HR
SLUG SIZE	=	*****	CC
CONCENTRATION	=	0.000	PERCENT NAOH
PV	=	594.000	CC
INIP	=	419.290	CC
PERMEABILITY	=	37.731	DARCYS
SWI	=	29.412	PERCENT
POROSITY	=	32.453	PERCENT
OIL VISCOSITY	=	502.000	CP

BREAK THROUGH = 82.00 CC 0.1380 PV 19.5568 PERCENT

DWP(CC)	WP(CC)	DNP(CC)	NP(CC)	PINP	WI(CC)	WI(PV)	WOR	DP(PST)	PH
0.00	0.00	43.00	43.00	10.25	43.00	0.07	0.00	*****	*****
0.00	0.00	39.00	82.00	19.55	82.00	0.13	0.00	*****	*****
3.00	3.00	12.50	94.50	22.53	97.50	0.16	0.24	*****	*****
5.50	8.50	11.50	106.00	25.28	114.50	0.19	0.47	*****	*****
21.40	29.90	23.60	129.60	30.90	159.50	0.26	0.90	*****	*****
41.00	70.90	19.00	148.60	35.44	219.50	0.36	2.15	*****	*****
34.00	104.90	12.69	161.30	38.46	266.20	0.44	2.67	*****	*****
38.50	143.40	10.00	171.30	40.85	314.70	0.52	3.85	*****	*****
49.00	192.40	13.00	184.30	43.95	376.70	0.63	3.76	*****	*****
39.20	231.60	6.59	190.89	45.52	422.50	0.71	5.93	*****	*****
35.50	267.10	6.29	197.19	47.03	464.30	0.78	5.63	*****	*****
28.00	295.10	4.00	201.19	47.98	496.30	0.83	7.00	*****	*****
45.20	340.30	6.80	207.99	49.60	548.30	0.92	6.64	*****	*****
55.00	395.30	5.00	212.99	50.80	608.30	1.02	11.00	*****	*****
52.80	448.10	4.20	217.19	51.80	665.30	1.12	12.57	*****	*****

TABLE D 6

RUN 2001
 TEMPERATURE = 85.000 DEGRFFS F
 RATE = 320.000 CC/HR
 SLUG SIZE = ***** CC
 CONCENTRATION = 0.000 PERCENT NAOH
 PV = 778.000 CC
 INIP = 711.000 CC
 PERMEABILITY = 27.225 DARCYS
 SWI = 8.611 PERCENT
 POROSITY = 41.651 PERCENT
 OIL VISCOSITY = 1105.000 CP

BREAK THROUGH = 68.00 CC 0.0874 PV 9.5639 PERCENT

DNP(CC)	WP(CC)	DNP(CC)	NP(CC)	PINP	WI(CC)	WI(PV)	WNR	NP(Psi)	PH
0.00	0.00	50.00	50.00	7.03	50.00	0.06	0.00	145.00	*****
0.70	0.70	18.30	68.30	9.60	69.00	0.08	0.03	125.00	*****
6.40	7.10	12.60	80.90	11.37	88.00	0.11	0.50	*****	*****
23.30	30.40	15.70	96.59	13.58	127.00	0.16	1.48	56.00	*****
29.00	59.40	12.00	108.59	15.27	168.00	0.21	2.41	*****	*****
33.50	92.90	8.29	116.89	16.44	209.80	0.26	4.03	*****	*****
38.00	130.90	9.00	125.89	17.70	256.80	0.33	4.22	35.00	*****
34.50	165.40	6.50	132.40	18.62	297.80	0.38	5.30	*****	*****
37.50	202.90	6.00	138.40	19.46	341.30	0.43	6.25	28.80	*****
43.00	245.90	6.00	144.40	20.30	390.30	0.50	7.16	26.00	*****
46.10	292.00	6.90	151.30	21.27	443.30	0.56	6.68	24.80	*****
49.50	341.50	6.50	157.80	22.19	499.30	0.64	7.61	22.50	*****
49.00	390.50	4.50	162.30	22.82	552.80	0.71	10.88	*****	*****
52.80	443.30	4.20	166.49	23.41	609.80	0.78	12.57	*****	*****
37.00	480.30	3.00	169.49	23.83	649.80	0.83	12.33	19.80	*****

TABLE 0 7

RUN 2002
 TEMPERATURE = 86.900 DEGREES F
 RATE = 320.000 CC/HR
 SLUG SIZE = *****
 CONCENTRATION = 0.000 PERCENT NAOH
 PV = 732.000 CC
 INIP = 685.000 CC
 PERMEABILITY = 24.503 DARCY
 SWI = 6.420 PERCENT
 POROSITY = 39.189 PERCENT
 OIL VISCOSITY = 1105.000 CP

BREAK THROUGH = 80.00 CC 0.1092 PV 11.6788 PERCENT

DWP(CC)	WP(CC)	ONP(CC)	NP(CC)	PINP	WI(CC)	WI(PV)	WOR	DP(Psi)	PH
0.00	0.00	38.00	38.00	5.54	38.00	0.05	0.00	*****	*****
0.00	0.00	32.00	70.00	10.21	70.00	0.09	0.00	*****	*****
0.10	0.10	13.90	83.90	12.24	84.00	0.11	0.00	*****	*****
3.50	3.60	11.50	95.40	13.92	99.00	0.13	0.30	65.00	*****
21.00	24.60	23.00	118.40	17.28	143.00	0.19	0.91	49.00	*****
30.00	54.60	20.50	138.90	20.27	193.50	0.26	1.46	42.50	*****
38.50	93.10	15.29	154.20	22.51	247.30	0.33	2.51	*****	*****
27.00	120.10	9.00	163.20	23.82	283.30	0.38	3.00	*****	*****
49.00	169.10	11.00	174.20	25.43	343.30	0.46	4.45	*****	*****
25.00	194.10	4.00	178.20	26.01	372.30	0.50	6.25	*****	*****
48.50	242.60	8.50	186.70	27.25	429.30	0.58	5.70	*****	*****

TABLE D A

RUN 2003
 TEMPERATURE = 87.000 DEGREES F
 RATE = 320.000 CC/HR
 SLUG SIZE = ***** CC
 CONCENTRATION = 0.000 PERCENT NAOH
 PV = 830.000 CC
 INIP = 771.000 CC
 PERMEABILITY = 28.372 DARCS
 SWI = 7.108 PERCENT
 POROSITY = 44.435 PERCENT
 OIL VISCOSITY = 1120.000 CP

BREAK THROUGH = 76.00 CC 0.0915 PV 9.8573 PERCENT

DWP(CC)	WP(CC)	ONP(CC)	NP(CC)	PINP	WI(CC)	WI(PV)	WOR	NP(Psi)	PH
0.00	0.00	47.00	47.00	6.09	47.00	0.05	0.00	*****	*****
0.00	0.00	15.00	62.00	8.04	62.00	0.07	0.00	*****	*****
0.00	0.00	14.00	76.00	9.85	76.00	0.09	0.00	75.00	*****
1.00	1.00	18.00	94.00	12.19	95.00	0.11	0.05	60.00	*****
15.00	16.00	25.20	119.20	15.46	135.20	0.16	0.59	*****	*****
29.80	45.80	13.40	132.60	17.19	178.40	0.21	2.22	*****	*****
21.50	67.30	8.50	141.10	18.30	208.40	0.25	2.52	43.00	*****
34.00	101.30	10.79	151.90	19.70	253.19	0.30	3.14	*****	*****
36.50	137.80	9.60	161.49	20.94	299.30	0.36	3.80	*****	*****
18.50	156.30	7.30	168.79	21.89	325.10	0.39	2.53	32.50	*****
40.00	196.30	7.89	176.69	22.91	372.99	0.44	5.06	*****	*****
43.50	239.80	8.00	184.69	23.95	424.49	0.51	5.43	*****	*****
41.80	281.60	5.40	190.09	24.65	471.69	0.56	7.74	25.20	*****
40.10	321.70	5.00	195.09	25.30	516.79	0.62	8.02	*****	*****
33.80	355.50	3.20	198.29	25.71	553.79	0.66	10.56	22.80	*****
49.00	404.50	6.00	204.29	26.49	608.79	0.73	8.16	*****	*****
49.00	453.50	5.00	209.29	27.14	662.79	0.79	9.80	*****	*****

TABLE D 9

RUN		2004		DEGREES F					
TEMPERATURE	=	87.000		CC/HR					
RATE	=	480.000		CC					
SLUG SIZE	=	*****		PERCENT NAOH					
CONCENTRATION	=	0.000		CC					
PV	=	830.000		CC					
INIP	=	656.500		DARCYS					
PERMEABILITY	=	28.375		PERCENT					
SWI	=	20.903		PERCENT					
POROSITY	=	44.431		CP					
OIL VISCOSITY	=	1120.000							
BREAK THROUGH = 58.00 CC 0.0698 PV 8.8347 PERCENT									
DWP(CC)	WP(CC)	ONP(CC)	NP(CC)	PINP	WI(CC)	WI(PV)	WOR	OP(PSI)	PH
0.00	0.00	39.50	39.50	6.01	39.50	0.04	0.00	160.00	*****
8.00	8.00	33.00	72.50	11.04	80.50	0.09	0.24	160.00	*****
19.00	27.00	29.50	102.00	15.53	129.00	0.15	0.64	160.00	*****
25.50	52.50	16.30	118.30	18.01	170.80	0.20	1.56	82.00	*****
27.00	79.50	11.50	129.80	19.77	209.30	0.25	2.34	74.00	*****
37.00	116.50	10.00	139.80	21.29	256.30	0.30	3.70	160.00	*****
44.00	160.50	12.00	151.80	23.12	312.30	0.37	3.66	160.00	*****
29.50	190.00	6.50	158.30	24.11	348.30	0.41	4.53	56.00	*****
36.00	226.00	7.00	165.30	25.17	391.30	0.47	5.14	44.00	*****
22.00	248.00	5.00	170.30	25.94	418.30	0.50	4.40	160.00	*****
36.50	284.50	5.50	175.80	26.77	460.30	0.55	6.63	39.00	*****
37.00	321.50	5.00	180.80	27.53	502.30	0.60	7.40	36.50	*****
34.50	356.00	4.50	185.30	28.22	541.30	0.65	7.66	160.00	*****

TABLE D12

RUN 3003
 TEMPERATURE = 85.000 DEGREES F
 RATE = 320.000 CC/HR
 SLUG SIZE = ***** CC
 CONCENTRATION = 1.000 PERCENT NAOH
 PV = 820.000 CC
 INIP = 756.000 CC
 PERMEABILITY = 27.475 DARCYS
 SWI = 7.804 PERCENT
 POROSITY = 43.900 PERCENT
 OIL VISCOSITY = 1105.000 CP

BREAK THROUGH = 171.80 CC 0.2095 PV 22.7248 PERCENT

DWP(CC)	WP(CC)	DNP(CC)	NP(CC)	PINP	WI(CC)	WI(PV)	WOR	NP(PSI)	PH
0.00	0.00	41.00	41.00	5.42	41.00	0.05	0.00	236.00	*****
0.00	0.00	39.80	80.80	10.68	80.80	0.09	0.00	*****	*****
0.00	0.00	46.00	126.80	16.77	126.80	0.15	0.00	233.00	*****
0.00	0.00	45.00	171.80	22.72	171.80	0.20	0.00	173.00	*****
0.80	0.80	14.20	186.00	24.60	186.80	0.22	0.05	*****	*****
3.50	4.30	17.50	203.50	26.91	207.80	0.25	0.20	146.00	*****
8.00	12.30	35.00	238.50	31.54	250.80	0.30	0.22	111.00	*****
20.00	32.30	20.00	258.50	34.19	290.80	0.35	1.00	*****	*****
29.50	61.80	17.50	276.00	36.50	337.80	0.41	1.68	84.00	12.60
30.50	92.30	12.00	288.00	38.09	380.30	0.46	2.54	76.00	12.75
27.00	119.30	10.50	298.50	39.48	417.80	0.50	2.57	61.00	*****
63.00	182.30	12.00	310.50	41.07	492.80	0.60	5.25	*****	12.82
54.50	236.80	5.00	315.50	41.73	552.30	0.67	10.90	42.00	12.80
33.00	269.80	3.79	319.30	42.23	589.10	0.71	8.68	40.00	*****
40.80	310.60	3.20	322.49	42.65	633.10	0.77	12.74	*****	12.89

TABLE 013

RUN 3004
 TEMPERATURE = 88.000 DEGR F
 RATE = 320.000 CC/HR
 SLUG SIZE = ***** CC
 CONCENTRATION = 0.100 PERCENT NAOH
 PV = 703.000 CC
 INIP = 670.000 CC
 PERMEABILITY = 21.827 DARCY
 SWI = 4.694 PERCENT
 POROSITY = 38.409 PERCENT
 OIL VISCOSITY = 990.000 CP

BREAK THROUGH = 170.50 CC 0.2425 PV 25.4477 PERCENT

DWP(CC)	WP(CC)	ONP(CC)	NP(CC)	PINP	WI(CC)	WI(PV)	WOR	OP(PSI)	PH
0.00	0.00	43.00	43.00	6.41	43.00	0.06	0.00	350.00	*****
0.00	0.00	46.00	89.00	13.28	89.00	0.12	0.00	264.00	*****
0.00	0.00	46.50	135.50	20.22	135.50	0.19	0.00	183.00	*****
0.20	0.20	34.80	170.30	25.41	170.50	0.24	0.00	155.00	*****
2.00	2.20	28.00	198.30	29.59	200.50	0.28	0.07	124.00	*****
21.00	23.20	25.60	223.90	33.41	247.10	0.35	0.82	*****	11.75
28.00	51.20	19.00	242.90	36.25	294.10	0.41	1.47	*****	11.90
33.00	84.20	13.50	256.40	38.26	340.60	0.48	2.44	41.00	11.92
40.00	124.20	13.00	269.40	40.20	393.60	0.55	3.07	42.00	*****
32.00	156.20	9.00	278.40	41.55	434.60	0.61	3.55	44.00	11.98
46.00	202.20	9.00	287.40	42.89	489.60	0.69	5.11	45.00	*****
52.00	254.20	6.00	293.40	43.79	547.60	0.77	8.66	44.00	11.98
38.00	292.20	5.00	298.40	44.53	590.60	0.84	7.60	44.00	*****

TABLE D14

RUN 4001									
TEMPERATURE =		RR.000		DEGRFES F					
RATE =		320.000		CC/HR					
SLUG SIZE =		250.000		CC					
CONCENTRATION =		0.100		PERCFNT NAOH					
PV =		727.000		CC					
INIP =		680.000		CC					
PERMEABILITY =		26.414		DARCYS					
SWI =		6.464		PERCFNT					
POROSITY =		39.716		PERCENT					
OIL VISCOSITY =		990.000		CP					
BREAK THROUGH = 172.00 CC 0.2365 PV 25.2941 PERCENT									
DWP(CC)	WP(CC)	DNP(CC)	NP(CC)	PIOP	WI(CC)	WI(PV)	WNR	NP(PSI)	PH
0.00	0.00	48.50	48.50	7.13	48.50	0.06	0.00	360.00	*****
0.00	0.00	51.00	99.50	14.63	99.50	0.13	0.00	280.00	*****
0.00	0.00	50.00	149.50	21.98	149.50	0.20	0.00	220.00	*****
0.00	0.00	22.50	172.00	25.29	172.00	0.23	0.00	170.00	*****
14.00	14.00	35.00	207.00	30.44	221.00	0.30	0.40	112.00	11.20
36.00	50.00	11.79	218.80	32.17	268.80	0.36	3.05	*****	10.65
38.00	88.00	8.50	227.30	33.42	315.30	0.43	4.47	49.00	*****
50.00	138.00	10.00	237.30	34.89	375.30	0.51	5.00	32.00	*****
51.00	189.00	5.00	242.30	35.63	431.30	0.59	10.20	26.00	9.91
40.00	229.00	2.00	244.30	35.92	473.30	0.65	20.00	22.00	*****

TABLE D15

4002		DEGR F.		PERCENT NANO	
TEMPERATURE =	87.000	CC/HR			
RATE =	320.000	CC			
SLUG SIZE =	325.000				
CONCENTRATION =	0.100				
PV =	809.000	CC			
INIP =	754.000	CC			
PERMEABILITY =	24.503	DARCYS			
SWI =	6.798	PERCENT			
POROSITY =	43.311	PERCENT			
OIL VISCOSITY =	1020.000	CP			
BREAK THROUGH = 153.00 CC		0.1891 PV		20.2917 PERCENT	
DWP(CC)	WP(CC)	DNP(CC)	NP(CC)	PINP	WI(CC)
0.00	0.00	46.50	46.50	6.16	46.50
0.00	0.00	44.00	90.50	12.00	90.50
0.00	0.00	48.00	138.50	18.36	138.50
1.00	1.00	17.50	156.00	20.68	157.00
14.00	15.00	35.50	191.50	25.39	206.50
19.80	34.80	25.20	216.70	28.74	251.50
19.00	53.80	23.00	239.70	31.79	293.50
20.00	73.80	21.00	260.70	34.57	334.50
25.00	98.80	21.00	281.70	37.36	380.50
25.50	124.30	14.00	295.70	39.21	420.00
41.00	165.30	14.50	310.20	41.14	475.50
46.80	212.10	10.70	320.89	42.55	533.00
39.50	251.60	7.50	328.39	43.55	580.00
40.80	292.40	5.20	333.59	44.24	626.00
		WNR		WI(PV)	
		0.00		0.05	
		0.00		0.11	
		0.00		0.17	
		0.05		0.19	
		0.39		0.25	
		0.78		0.31	
		0.82		0.36	
		0.95		0.41	
		1.19		0.47	
		1.82		0.51	
		2.82		0.58	
		4.37		0.65	
		5.26		0.71	
		7.84		0.77	
		DP(PSI)		PH	
		265.00		*****	
		93.50		*****	
		*****		*****	
		*****		*****	
		90.00		11.55	
		94.00		11.70	
		*****		11.98	
		98.00		11.74	
		*****		*****	
		70.00		11.30	
		*****		*****	
		38.00		10.25	
		25.00		*****	
		*****		9.90	

TABLE 016

4003

RUN TEMPERATURE = 87.000 DEGRFFS F
 RATE = 320.000 CC/HR
 SLUG SIZE = 280.000 CC
 CONCENTRATION = 0.100 PERCENT NAOH
 PV = 812.000 CC
 INIP = 762.000 CC
 PERMEABILITY = 22.461 DARCS
 SWI = 6.157 PERCENT
 POROSITY = 43.472 PERCENT
 OIL VISCOSITY = 1020.000 CP

BREAK THROUGH = 188.00 CC 0.2315 PV 24.6719 PERCENT

DWP (CC)	WP (CC)	DNP (CC)	NP (CC)	PI NP	WI (CC)	WI (PV)	WNR	NP (PSI)	PH
0.00	0.00	46.00	46.00	6.03	46.00	0.05	0.00	340.00	#####
0.00	0.00	46.00	92.00	12.07	92.00	0.11	0.00	#####	#####
0.00	0.00	47.00	139.00	18.24	139.00	0.17	0.00	240.00	#####
0.00	0.00	45.00	184.00	24.14	184.00	0.22	0.00	170.00	#####
1.00	1.00	22.00	206.00	27.03	207.00	0.25	0.04	150.00	#####
13.00	14.00	39.00	245.00	32.15	259.00	0.31	0.33	#####	11.30
18.00	32.00	14.00	259.00	33.98	291.00	0.35	1.28	75.00	11.05
32.00	64.00	13.00	272.00	35.69	336.00	0.41	2.46	#####	10.60
25.00	89.00	5.00	277.00	36.35	366.00	0.45	5.00	44.00	10.10
54.50	143.50	7.50	284.50	37.33	428.00	0.52	7.26	#####	#####
39.00	182.50	4.00	288.50	37.86	471.00	0.58	9.75	24.00	9.45

TABLE 017

RUN 4004
 TEMPERATURE =
 RATE =
 SLUG SIZE =
 CONCENTRATION =
 PV =
 IDIP =
 PERMEABILITY =
 SWI =
 POROSITY =
 OIL VISCOSITY =

87.000 DEGR FES F
 320.000 CC/HR
 105.000 CC
 0.100 PERCENT NAOH
 805.000 CC
 765.000 CC
 24.503 DARCYS
 4.968 PERCENT
 43.097 PERCENT
 1020.000 CP

BREAK THROUGH = 119.00 CC 0.1478 PV 15.5555 PERCENT

DWP(CC)	WP(CC)	DNP(CC)	NP(CC)	PIOP	WI(CC)	WI(PV)	WNR	NP(PSI)	PH
0.00	0.00	51.00	51.00	6.66	51.00	0.06	0.00	250.00	#####
0.00	0.00	53.00	104.00	13.59	104.00	0.12	0.00	130.00	#####
0.50	0.50	26.00	130.00	16.99	130.50	0.16	0.01	125.00	#####
14.00	14.50	32.00	162.00	21.17	176.50	0.21	0.43	124.00	9.65
23.50	38.00	23.00	185.00	24.18	223.00	0.27	1.02	#####	9.08
30.20	68.20	17.80	202.80	26.50	271.00	0.33	1.69	46.00	#####
24.80	93.00	7.00	209.80	27.42	302.80	0.37	3.54	#####	8.85
36.00	129.00	7.79	217.60	28.44	346.60	0.43	4.61	30.00	#####
52.50	181.50	5.50	223.10	29.16	404.60	0.50	9.54	26.00	8.78
36.50	218.00	7.00	230.10	30.07	448.10	0.55	5.21	21.00	#####
39.00	257.00	3.50	233.60	30.53	490.60	0.60	11.14	21.00	#####
47.00	304.00	6.50	240.10	31.38	544.10	0.67	7.23	20.00	8.75

TABLE 01A

RUIN	4005	
TEMPERATURE =	86.000	DEGRFFS F
RATE =	320.000	CC/HR
SLUG SIZE =	402.000	CC
CONCENTRATION =	0.100	PERCENT NAOH
PV =	749.000	CC
INIP =	698.000	CC
PERMEABILITY =	21.827	DARCY
SWI =	6.809	PERCENT
POROSITY =	40.922	PERCENT
OIL VISCOSITY =	1055.000	CP

BREAK THROUGH = 150.80 CC 0.2013 PV 21.6045 PERCENT									
DWP(CC)	WP(CC)	DNP(CC)	NP(CC)	PIOP	WI(CC)	WI(PV)	WOR	NP(PST)	PH
0.00	0.00	42.50	42.50	6.08	42.50	0.05	0.00	350.00	*****
0.00	0.00	44.50	87.00	12.46	87.00	0.11	0.00	274.00	*****
0.00	0.00	48.80	135.80	19.45	135.80	0.18	0.00	190.00	*****
0.00	0.00	15.00	150.80	21.60	150.80	0.20	0.00	174.00	*****
8.30	8.30	35.70	186.50	26.71	194.80	0.26	0.23	135.00	10.70
20.00	28.30	23.50	210.00	30.08	238.30	0.31	0.85	107.00	11.40
26.00	54.30	16.80	226.80	32.49	281.10	0.37	1.54	77.00	11.75
34.00	88.30	15.00	241.80	34.64	330.10	0.44	2.26	62.00	11.80
35.00	123.30	14.00	255.80	36.64	379.10	0.50	2.50	58.00	11.85
34.00	157.30	11.50	267.30	38.29	424.60	0.56	2.95	60.00	11.85
33.00	190.30	9.50	276.80	39.65	467.10	0.62	3.47	59.00	11.65
36.00	226.30	12.00	288.80	41.37	515.10	0.68	3.00	59.00	11.10
27.00	253.30	9.00	297.80	42.66	551.10	0.73	3.00	55.00	10.95
32.50	285.80	10.29	308.10	44.14	593.90	0.79	3.15	50.00	*****
42.00	327.80	12.00	320.10	45.85	647.90	0.86	3.50	40.00	10.35
26.00	353.80	6.50	326.60	46.79	680.40	0.90	4.00	31.00	10.30

TABLE D19

RUN	4006	
TEMPERATURE F	=	86.000
RATE	=	320.000
SLUG SIZE	=	105.000
CONCENTRATION	=	1.000
PV	=	801.000
INIP	=	758.000
PERMEABILITY	=	22.650
SWI	=	5.368
POROSITY	=	42.883
OIL VISCOSITY	=	1055.000

BREAK THROUGH = 133.00 CC 0.1660 PV 17.5461 PERCENT

DWP(CC)	WP(CC)	DNP(CC)	NP(CC)	PINP	WI(CC)	WI(PV)	WOR	NP(PSI)	PH
0.00	0.00	47.50	47.50	6.26	47.50	0.05	0.00	335.00	*****
0.00	0.00	47.50	95.00	12.53	95.00	0.11	0.00	240.00	*****
0.00	0.00	35.00	137.00	17.15	130.00	0.16	0.00	158.00	*****
7.00	7.00	44.00	174.00	22.95	181.00	0.22	0.15	150.00	*****
29.00	36.00	36.00	210.00	27.70	246.00	0.30	0.80	*****	11.55
35.00	71.00	32.00	242.00	31.92	313.00	0.39	1.09	*****	11.35
31.00	102.00	16.50	258.50	34.10	360.50	0.45	1.87	105.00	11.10
27.00	129.00	11.00	269.50	35.55	398.50	0.49	2.45	80.00	*****
35.00	164.00	14.00	283.50	37.40	447.50	0.55	2.50	78.00	10.92
39.00	203.00	12.50	296.00	39.05	499.00	0.62	3.12	68.00	*****
34.00	237.00	7.00	303.00	39.97	540.00	0.67	4.85	60.00	10.50
44.00	281.00	8.00	311.00	41.02	592.00	0.73	5.50	44.00	*****

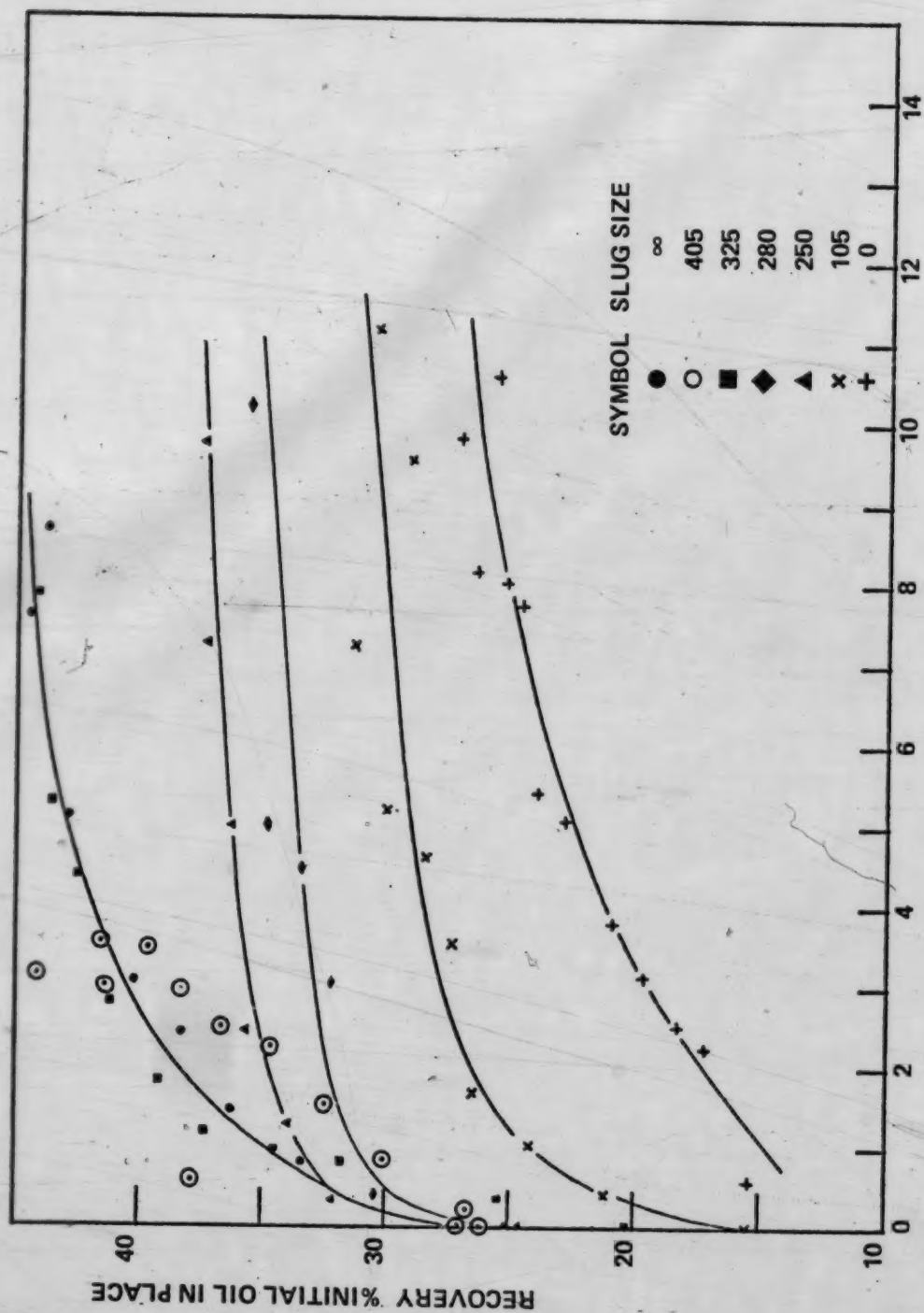


FIGURE D-1 RECOVERY AS A FUNCTION OF WATER OIL RATIO FOR DIFFERENT SLUG SIZES

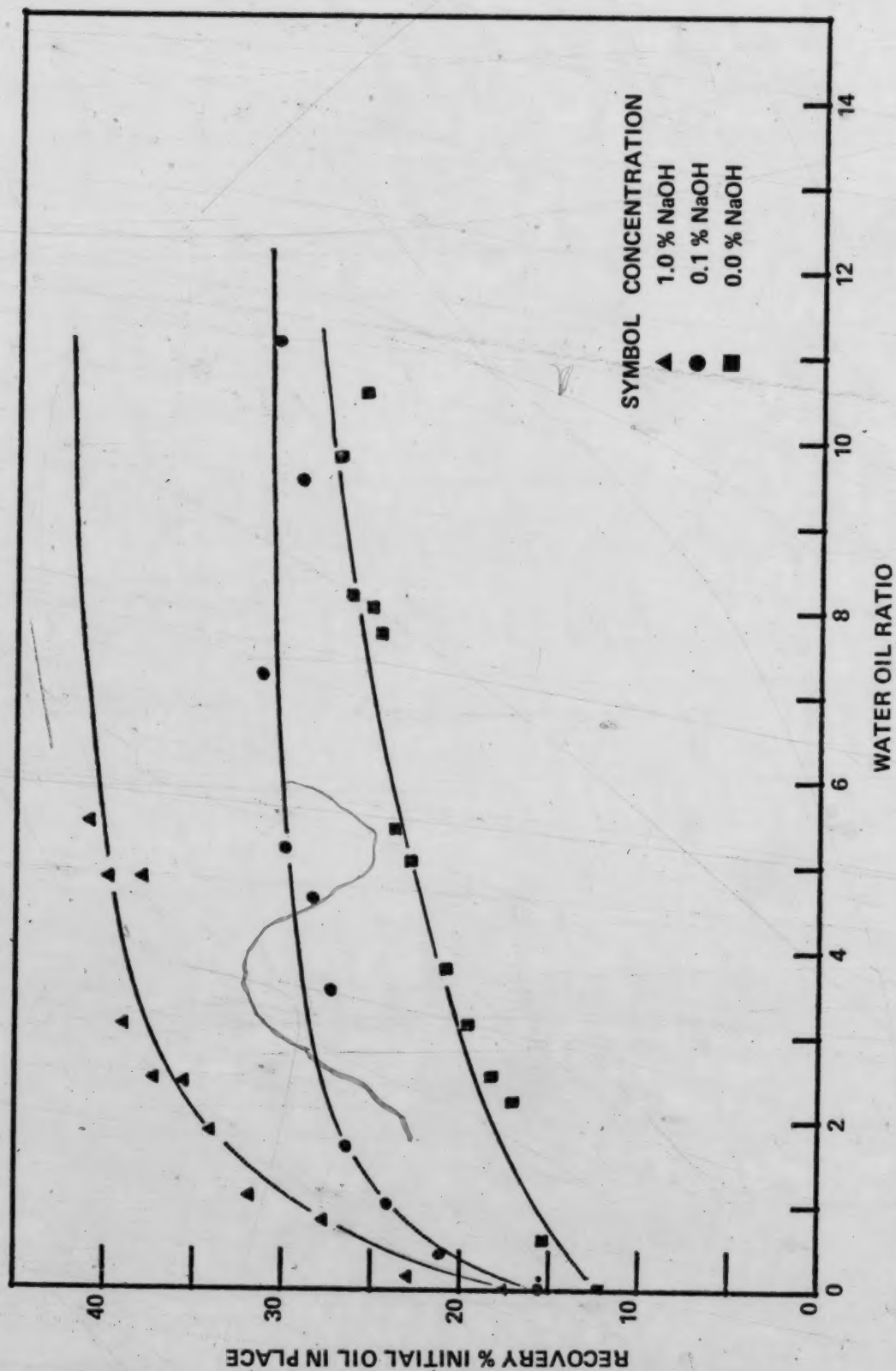


FIGURE D-2 COMPARISON OF RECOVERIES AND WATER OIL RATIOS OF 105 CC SLUGS WITH DIFFERENT SODIUM HYDROXIDE CONCENTRATION.

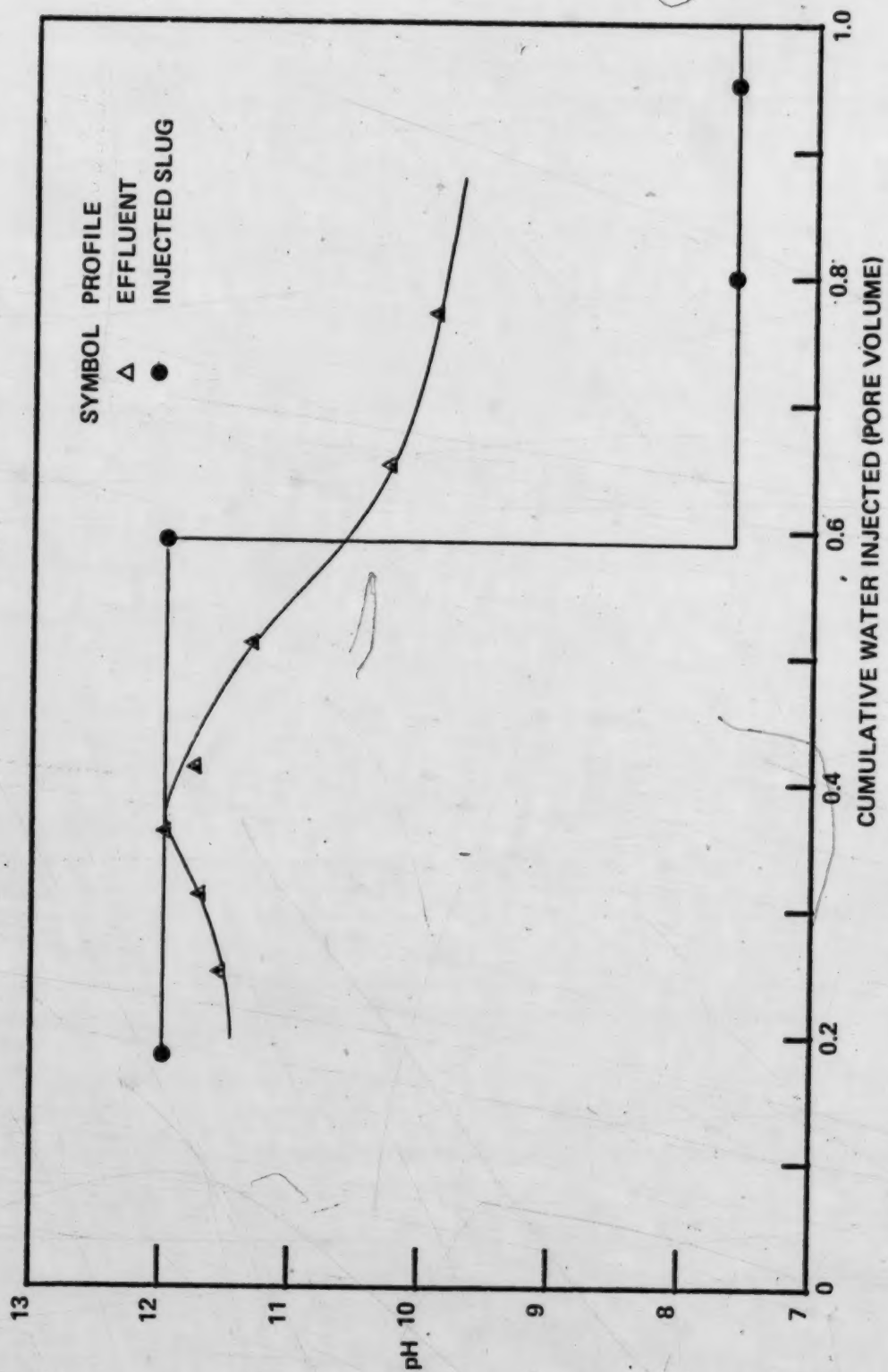


FIGURE D-3 IDEALIZED CONTRAST OF INJECTED AND PRODUCED pH PROFILE OF 325 cc SLUG OF 0.1 PERCENT BY WEIGHT SODIUM HYDROXIDE

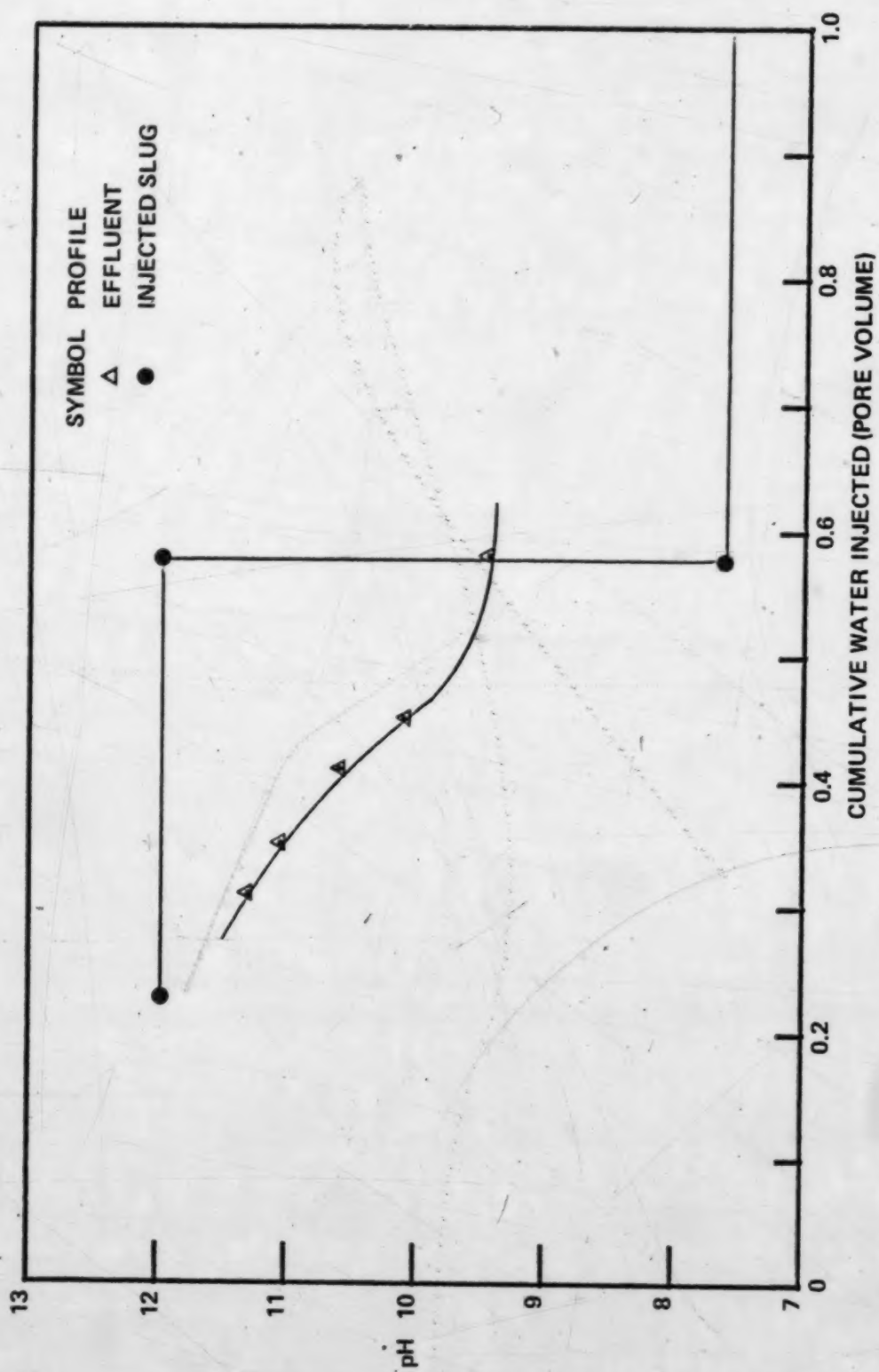


FIGURE D-4 IDEALIZED CONTRAST OF INJECTED AND PRODUCED pH PROFILE OF 280 cc SLUG OF 0.1 PERCENT BY WEIGHT SODIUM HYDROXIDE

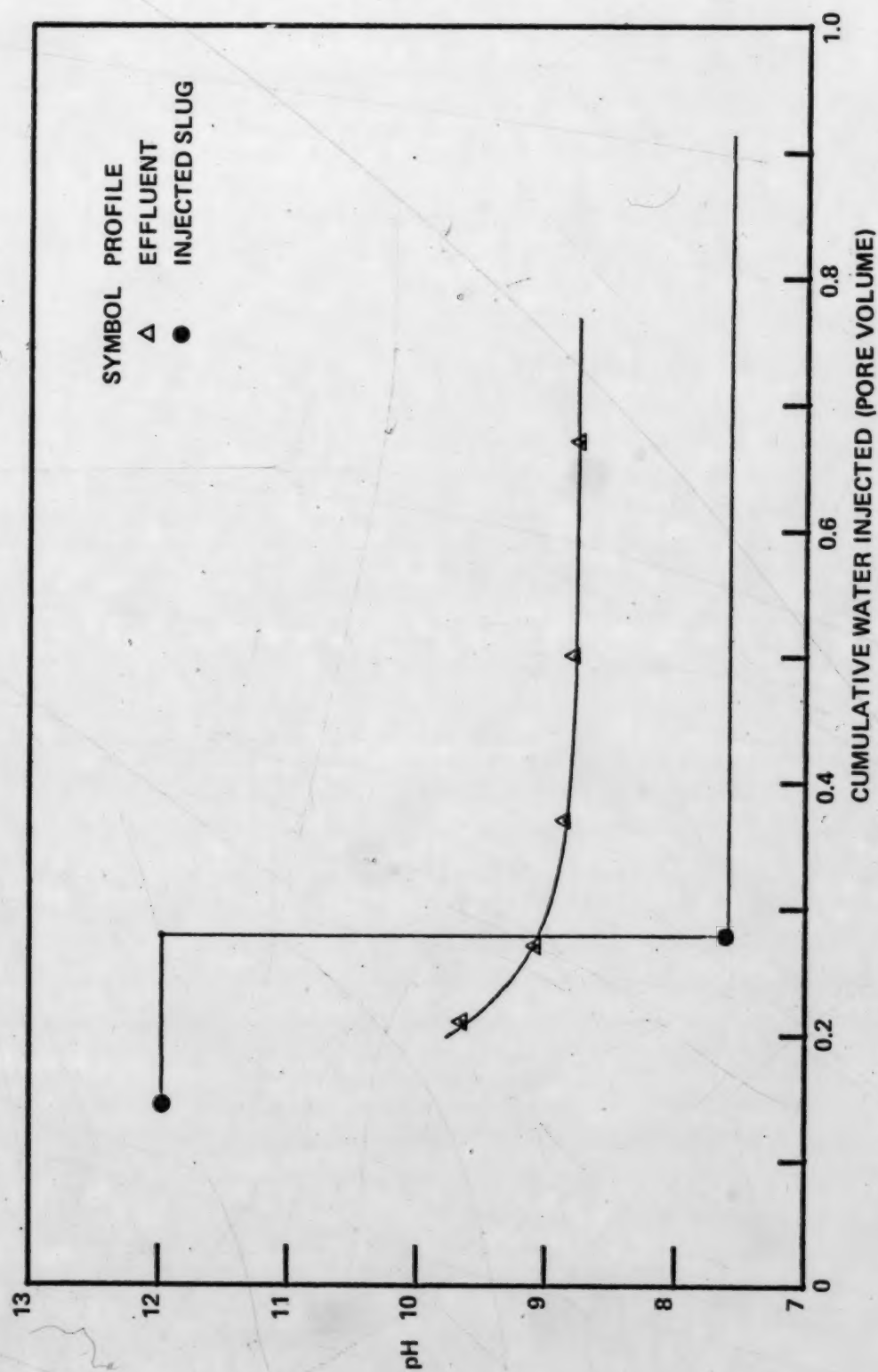


FIGURE D-5 IDEALIZED CONTRAST OF INJECTED AND PRODUCED pH PROFILE OF 105 cc SLUG OF 0.1 PERCENT BY WEIGHT SODIUM HYDROXIDE

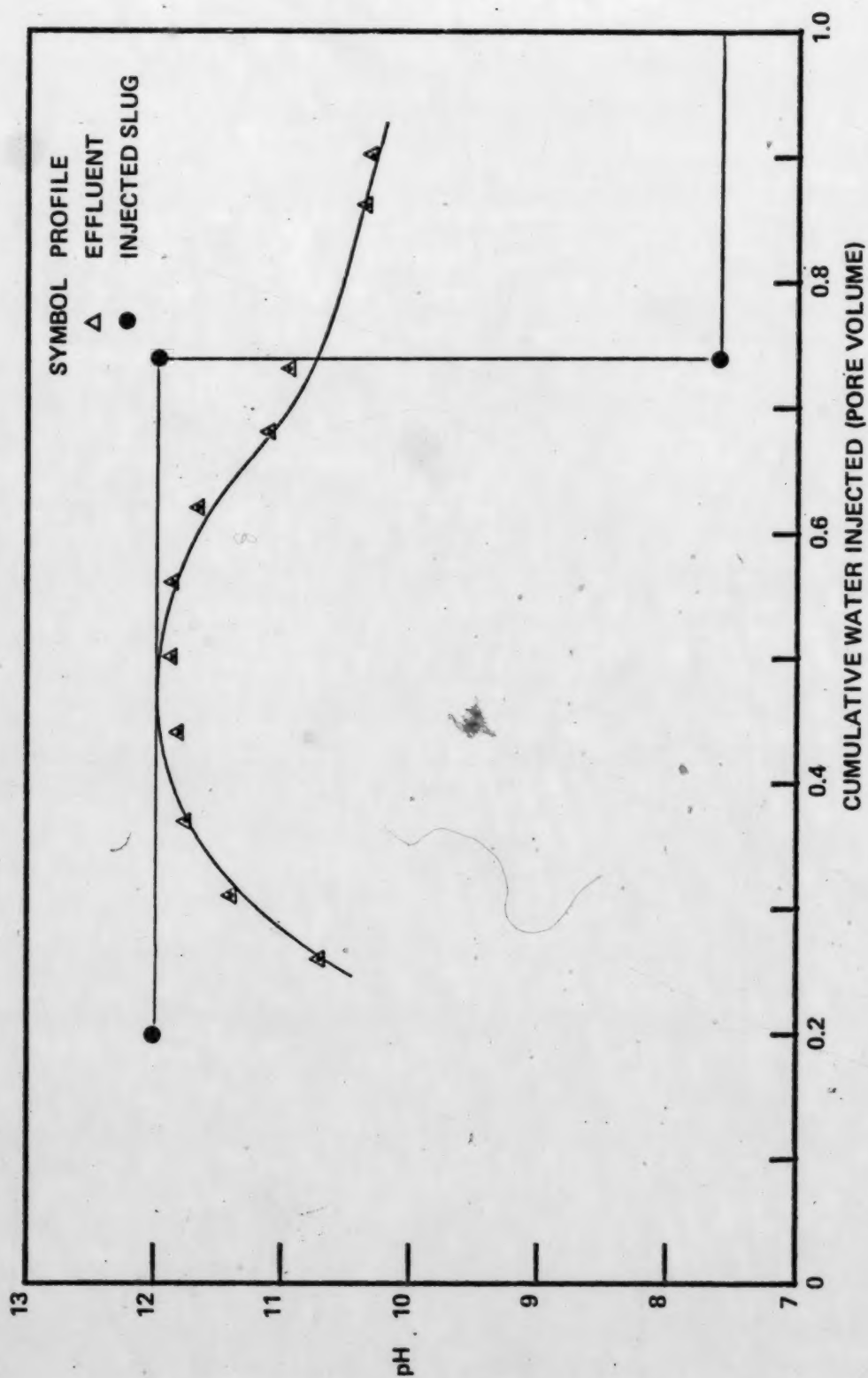


FIGURE D-6 IDEALIZED CONTRAST OF INJECTED AND PRODUCED pH PROFILE OF 402 cc SLUG OF 0.1 PERCENT BY WEIGHT SODIUM HYDROXIDE

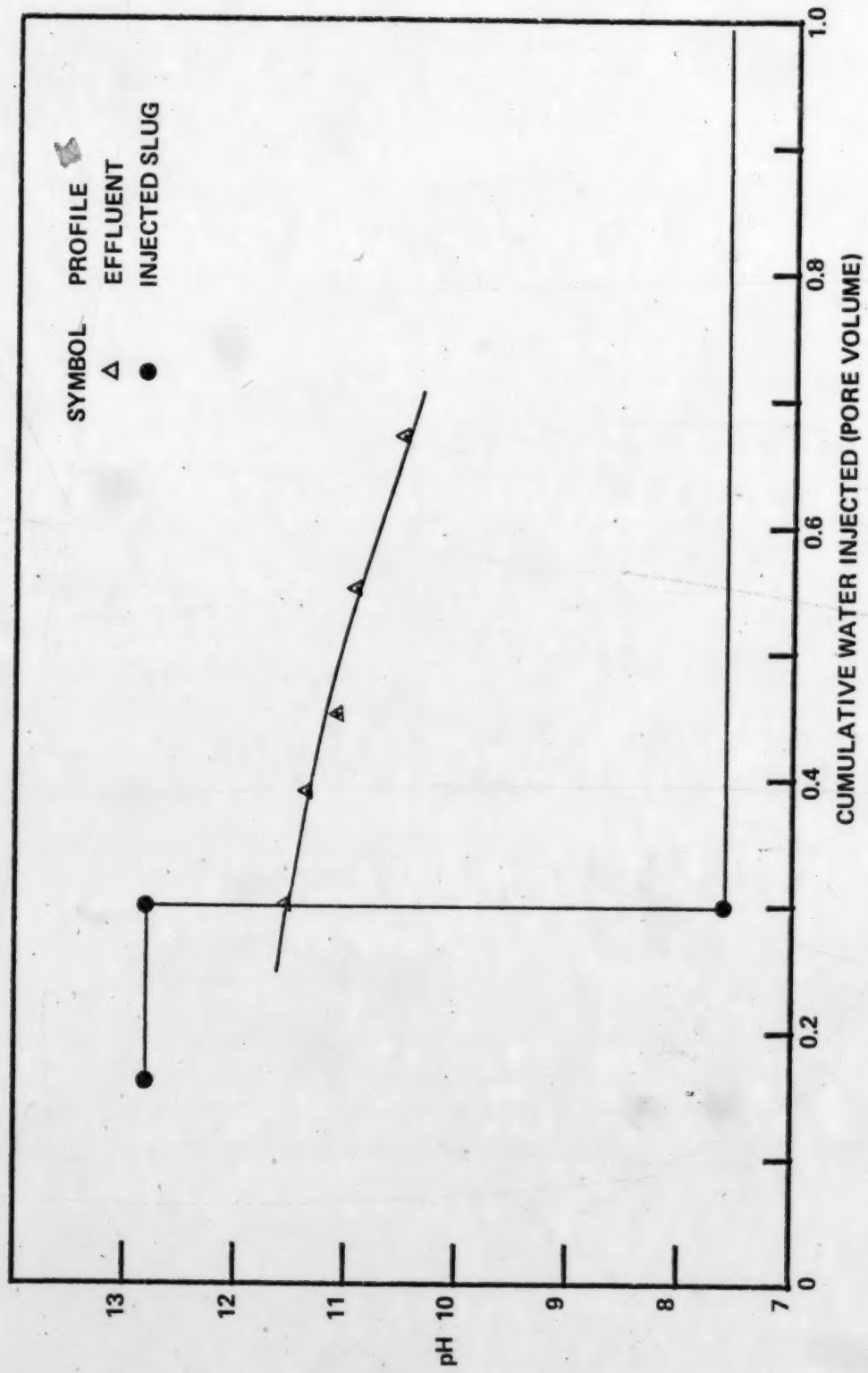


FIGURE D-7 IDEALIZED CONTRAST OF INJECTION AND PRODUCTION pH PROFILE OF 105 cc SLUG OF 1.0 PERCENT BY WEIGHT SODIUM HYDROXIDE

APPENDIX E

RELATIVE PERMEABILITY DETERMINATIONS
FROM EXPERIMENTAL DATA

RELATIVE PERMEABILITY CALCULATIONS

The Welge integration of the Buckley Leveritt equation was used to calculate the relative permeabilities from displacement data as suggested by Collins¹⁰.

$$\frac{K_w}{K_{nw}} = \frac{\mu_w}{\mu_{nw}} \frac{1-f_w}{f_{nw}} \quad \text{E-1}$$

where:

μ_w = viscosity of wetting phase, cp,

μ_{nw} = viscosity of non-wetting phase, cp,

K_w = permeability of wetting phase, md,

K_{nw} = permeability of non-wetting phase, md,

f_{nw} = non-wetting phase fractional flow, and

f_w = wetting phase fractional flow.

The saturation corresponding to this ratio is the instantaneous value at the outflow phase. This saturation is calculated at the middle of the production interval by the use of Equations E-2 and E-3.

$$S_{wa} = \frac{N_p - \frac{1}{2} \Delta N_p}{PV} + S_{wi} \quad \text{E-2}$$

$$S_{wd} = S_{wa} - f_o \frac{W_p + N_p - \frac{1}{2}(N_p + \Delta W_p)}{PV} \quad E-3$$

Where:

- S_{wa} = average water saturation,
- N_p = cumulative oil production, cc,
- ΔN_p = oil production during time step, cc,
- S_{wi} = initial water saturation
- PV = core pore volume, cc,
- S_{wd} = average water saturation in middle of time step
- f_o = fractional flow, oil
- W_p = cumulative water production, cc,
- ΔW_p = water production during time step, cc,

Results of the relative permeability calculations are presented in Table E-1 to E-3.

TABLE E-1
RELATIVE PERMEABILITY OF TEST No. 6

ΔN_p (cc)	ΔW_p (cc)	N_p (cc)	W_p (cc)	WOR	f_o	$\frac{K_w}{K_o}$	S_{wa}	S_{wd}
50.00	0.00	50.00	0.00	0.000	1.0000	0.00000	0.11825	0.08611
18.30	0.70	68.30	0.70	0.038	0.9631	0.00003	0.16214	0.08848
12.60	6.40	80.90	7.10	0.507	0.6631	0.00045	0.18200	0.11509
15.70	23.30	96.59	30.40	1.484	0.4025	0.00132	0.20019	0.14456
12.00	29.00	108.59	59.40	2.416	0.2926	0.00216	0.21799	0.16250
8.29	33.50	116.89	92.90	4.036	0.1985	0.00361	0.23104	0.18282
9.00	38.00	125.89	130.90	4.222	0.1914	0.00378	0.24215	0.18473
6.50	34.50	132.40	165.40	5.307	0.1585	0.00475	0.25212	0.19561
6.00	37.50	138.40	202.90	6.250	0.1379	0.00559	0.26015	0.20350
6.00	43.00	144.40	245.90	7.166	0.1224	0.00642	0.26786	0.21029
6.90	46.10	151.30	292.00	6.681	0.1301	0.00598	0.27615	0.20641
6.50	49.50	157.80	341.50	7.615	0.1160	0.00682	0.28476	0.21445
4.50	49.00	162.30	390.50	10.888	0.0841	0.00975	0.29183	0.23496
4.20	52.80	166.49	443.30	12.571	0.0736	0.01126	0.29742	0.24237
3.00	37.00	169.49	480.30	12.333	0.0750	0.01104	0.30205	0.24134

TABLE E-2
RELATIVE PERMEABILITY OF TEST No. 8

ΔN_p (cc)	ΔW_p (cc)	N_p (cc)	W_p (cc)	WOR	f_o	$\frac{K_w}{K_o}$	S_{wa}	S_{wd}
47.00	0.00	47.00	0.00	0.000	1.0000	0.00000	0.09939	0.07108
15.00	0.00	62.00	0.00	0.000	1.0000	0.00000	0.13674	0.07108
14.00	0.00	76.00	0.00	0.000	1.0000	0.00000	0.15421	0.07108
18.00	1.00	94.00	1.00	0.055	0.9473	0.00004	0.17349	0.07590
25.20	15.00	119.20	16.00	0.595	0.6268	0.00052	0.19951	0.11258
13.40	29.80	132.60	45.80	2.223	0.3101	0.00196	0.22277	0.16417
8.50	21.50	141.10	67.30	2.529	0.2833	0.00223	0.23596	0.16994
10.79	34.00	151.90	101.30	3.148	0.2410	0.00278	0.24759	0.18055
9.60	36.50	161.49	137.80	3.802	0.2082	0.00336	0.25987	0.19056
7.30	18.50	168.79	156.30	2.534	0.2829	0.00224	0.27006	0.16363
7.89	40.00	176.69	196.30	5.063	0.1649	0.00447	0.27921	0.20985
8.00	43.50	184.69	239.80	5.437	0.1553	0.00480	0.28879	0.21416
5.40	41.80	190.09	281.60	7.740	0.1144	0.00684	0.29686	0.23510
5.00	40.10	195.09	321.70	8.020	0.1108	0.00708	0.30313	0.23711
3.20	33.80	198.29	355.50	10.562	0.0864	0.00933	0.30807	0.25229
6.00	49.00	204.29	404.50	8.166	0.1090	0.00721	0.31361	0.23721
5.00	49.00	209.29	453.50	9.800	0.0925	0.00866	0.32024	0.24931

TABLE E-3
RELATIVE PERMEABILITY OF TEST No. 9

ΔN_p (cc)	ΔW_p (cc)	N_p (cc)	W_p (cc)	WOR	f_o	$\frac{K_w}{K_o}$	S_{wa}	S_{wd}
39.50	0.00	39.50	0.00	0.000	1.0000	0.00000	0.23283	0.20903
33.00	8.00	72.50	8.00	0.242	0.8048	0.00021	0.27650	0.21832
29.50	19.00	102.00	27.00	0.644	0.6082	0.00056	0.31415	0.23739
16.30	25.50	118.30	52.50	1.564	0.3899	0.00138	0.34174	0.27132
11.50	27.00	129.80	79.50	2.347	0.2987	0.00207	0.35849	0.29009
10.00	37.00	139.80	116.50	3.700	0.2127	0.00327	0.37144	0.31176
12.00	44.00	151.80	160.50	3.666	0.2142	0.00324	0.38469	0.31129
6.50	29.50	158.30	190.00	4.538	0.1805	0.00401	0.39584	0.32399
7.00	36.00	165.30	226.00	5.142	0.1627	0.00454	0.40397	0.33144
5.00	22.00	170.30	248.00	4.400	0.1851	0.00388	0.41120	0.32088
5.50	36.50	175.80	284.50	6.636	0.1309	0.00586	0.41753	0.34822
5.00	37.00	180.80	321.50	7.400	0.1190	0.00654	0.42385	0.35482
4.50	34.50	185.30	356.00	7.666	0.1153	0.00677	0.42957	0.35703

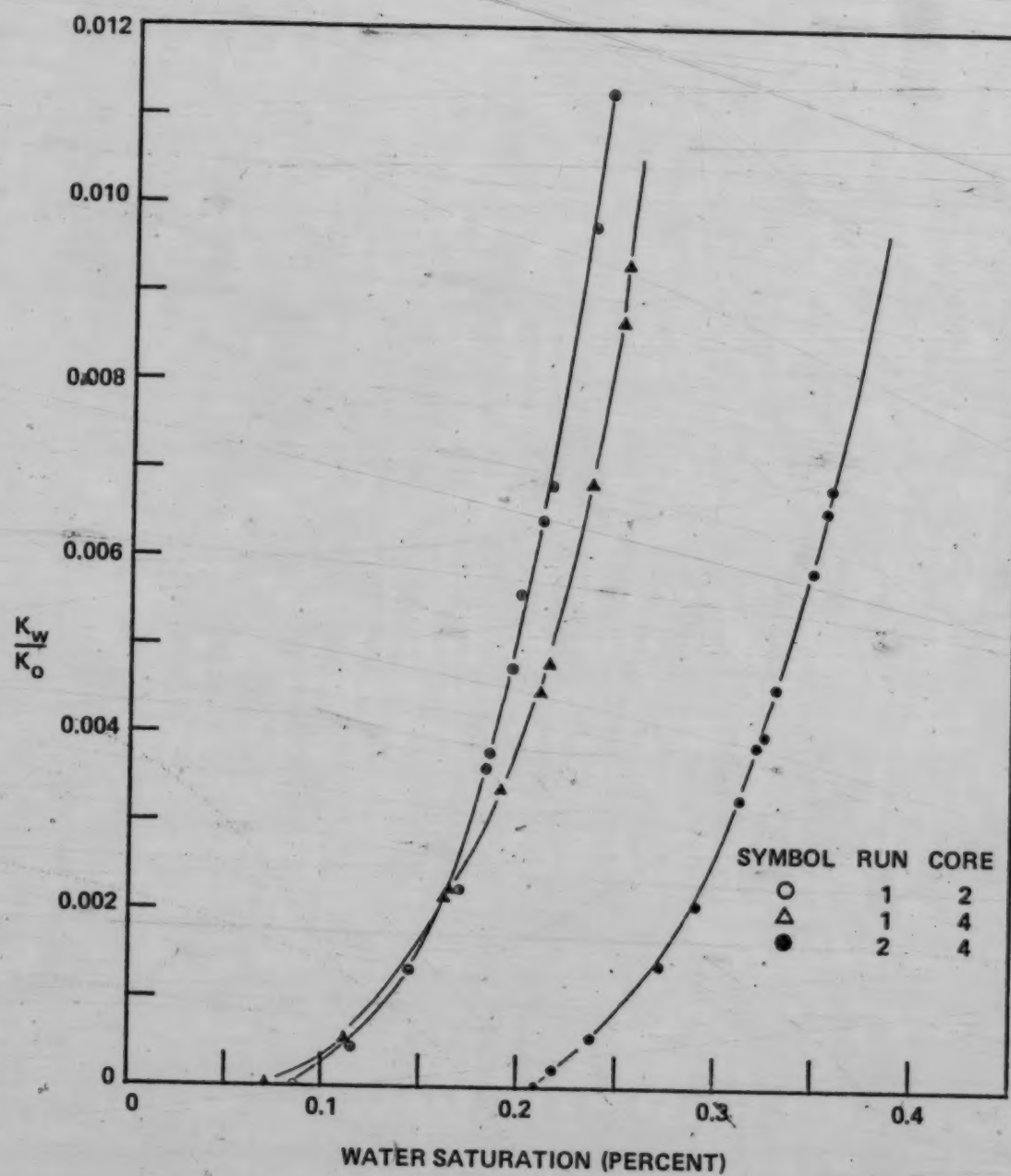


FIGURE E-1 THE EFFECT ON RELATIVE PERMEABILITY OF MULTIPLE DISPLACEMENT TESTS ON A CORE

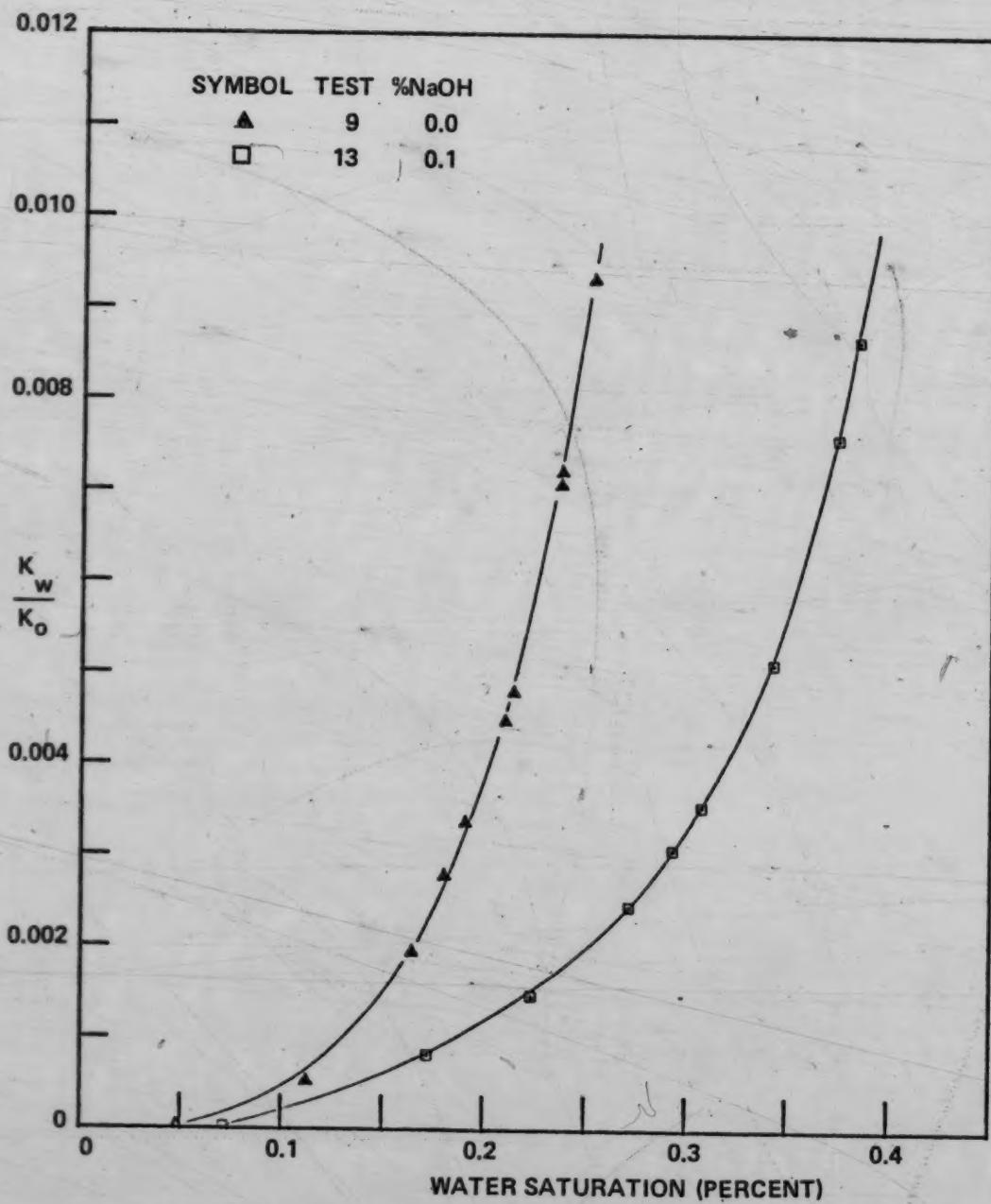


FIGURE E-2 THE EFFECT OF SODIUM HYDROXIDE ON RELATIVE PERMEABILITY

APPENDIX F

APPLICATION OF EXPERIMENTAL RESULTS
TO AN IDEALIZED FIELD CASE

IDEALIZED OIL FIELD PROJECT

Initial Conditions

$\phi = 40\%$ Area = 40 acres $B_{oi} = 1.25$	$h = 10 \text{ feet}$ $S_{wi} = 10 \text{ percent}$ $*\rho_w = 1.0859$ *0.1 percent by weight sodium hydroxide.
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Initial Oil-In-Place

$$N = \frac{7758 \phi (1 - S_{wi}) \text{ Area } h}{B_{oi}}$$

$$N = \frac{7758 (0.4) (1 - 0.1) (40) (10)}{1.25}$$

$$N = 893,721 \text{ ST Bbls.}$$

Linear Laboratory Model

Initial Oil-In-Place	750 cc
Slug Size	300 cc
Concentration Sodium Hydroxide	0.1 percent by weight
Recovery at W.O.R. of 10	43% of I.O.I.P.

$$\text{Recovery Factor} = \frac{\text{Oil Recovered}}{\text{Sodium Hydroxide Injected}}$$

$$\text{Recovery Factor} = \frac{750\text{cc}(0.43)}{300\text{cc}(0.001)(1.0839)} = 990 \frac{\text{cc oil}}{\text{gm sodium hydroxide}}$$

$$\text{Recovery Factor} = 2.519 \text{ Bbls. Oil/lb. Sodium Hydroxide}$$

Conventional Water Flood Recovery

Recovery of I.O.I.P.

$$(\text{At W.O.R.} = 10) = 10\%$$

$$893,721 \times 0.1 = 89,372 \text{ ST Bbls.}$$

Sodium Hydroxide Slug Field Project Recovery (assume
linear flow, 50% volumetric sweep)

$$893,721 \times 0.43 \times 0.5 = 192,150 \text{ STB}$$

Sodium Hydroxide Required

$$192,150 / 2.519 = 67,617 \text{ lbs.}$$

Increased Recovery Using Sodium Hydroxide

$$192,150 - 89,372 = 107,778 \text{ STB}$$

Slug Volume Required

225,000 Bbls. water

Idealized Injection Rates

1,000 Bbls. water per day

Time Required to Inject Slug

$$\frac{225,000}{1,000} = 225 \text{ days}$$

Economic Estimate

Sodium Hydroxide cost (50¢/lb.) 67,617 lbs. = \$33,809